Magnetic Properties of the Alternating-chain Compounds $Cu(bipy)X_2$ (bipy = 2,2'-bipyridine, X = Br or Cl)†

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Magnetic susceptibility data have been collected for the complexes $Cu(bipy)X_2$ (bipy = 2,2'-bipyridine, X = Br or Cl) in the temperature range 2–300 K. The data were analysed in terms of the alternating-chain Heisenberg exchange model to yield $J = -0.83$ cm^{-1} and $\alpha = 0.22$ for the chloro complex and $J = -1.00$ cm^{-1} and $\alpha = 0.26$ for the bromo complex. This fit is compared with the values obtained by using the Bleaney–Bowers equation for dimeric copper(II) compounds.

The structural and magnetic properties of dimeric bis(μ-chloro)-bridged copper(II) complexes have been intensively studied.[1–5] The metal ions in most of these complexes are antiferromagnetically exchange coupled, although some examples of triplet ground state, ferromagnetically coupled systems are known.[4] There is less information on the structural and magnetic properties of dimeric bis(μ-bromo)-bridged copper dimers.[6,7]

For polymeric bis(μ-chloro)- and bis(μ-bromo)-bridged complexes two kinds of structures are known: uniform and alternating chains.[8] *catena*-Dichloro(diphenylethanedione dioxime)-copper(II) has a uniformly spaced, infinite-chain structure in which the monomeric units are stacked by bis(μ-chloro) bridges to yield a zigzag structure.[9] A polymeric zigzag chain structure is also present in *catena*-dibromo(cyclohexane-1,2-dione dioxime)copper(II), but the copper ions are not bromo-bridged in this compound. Instead the chain is propagated by co-ordination of oxime oxygens.[9] Other examples of alternating chain structures with bridging ligands different from halogen atoms are known.[10–13]

On the basis of their magnetic properties the following compounds have been suggested to have alternately spaced linear-chain structures at low temperatures: *catena*-di-μ-bromo-bis-(*N*-methylimidazole)copper(II)[14] and *catena*-di-μ-chloro-bis(4-methylpyridine)copper(II). These compounds have uniformly spaced linear-chain structures at room temperature.[14,15] *catena*-Dichloro(3,6-dithiaoctane)copper(II) has an alternately spaced structure at 140 K, and its magnetic properties were explained by Heisenberg alternating-chain exchange theory.[16]

Experimental

The complexes were prepared by addition of anhydrous $CuCl_2$ or $CuBr_2$ (1 mmol) to a solution containing the 2,2'-bipyridine(bipy) (1 mmol) in freshly distilled methanol. The resultant solution was refluxed, and a green microcrystalline solid formed when the reaction mixture was cooled.

Magnetic susceptibility measurements were performed in the temperature range 2–300 K using a SHE, Corp VTS variable-temperature magnetometer (model 906). Magnetization at low temperatures was shown to be linear with applied fields from 1 to 10 kG. Susceptibility measurements were carried out at 1 kG. A metallic sample holder with a known temperature-independent paramagnetic signal was used. The data were corrected to compensate for the diamagnetism of the constituent atoms (Pascal constants) and for the temperature-independent paramagnetism of copper(II).[17]

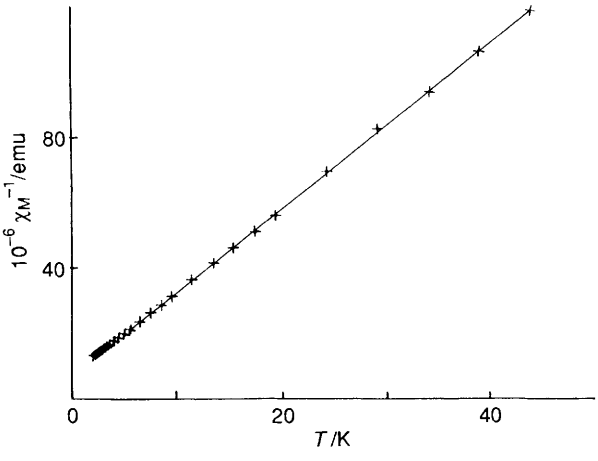

Fig. 1 Corrected magnetic susceptibility *vs.* temperature for $Cu(bipy)Cl_2$. The solid line was generated by the expression corresponding to the Heisenberg alternating-chain model

The data were analysed in terms of the alternating-chain Heisenberg exchange model.[13,18] The theoretical molar susceptibility, χ_M, the J and g values were also calculated from a non-linear least-squares fit of the Bleaney–Bowers equation to the experimental data, considering a dimeric model.[19] The corresponding formulas are analysed in the text. The function minimized in all curve-fitting procedures was $F = \sum_i (\chi_i^{obs} - \chi_i^{calc})^2/(\chi_i^{obs})^2$.

Results and Discussion

We have found that $Cu(bipy)X_2$ (X = Cl or Br) have an alternately spaced polymeric structure at room temperature.[20] Therefore the magnetic susceptibility of the complexes was measured to determine whether antiferromagnetic interactions could be detected at low temperatures.

The magnetic data displayed in Fig. 1 were collected in the temperature range 2–300 K. The susceptibility data for both complexes obey the Curie–Weiss law and data collected in the

† *Non-SI unit employed:* G = 10^{-4} T.

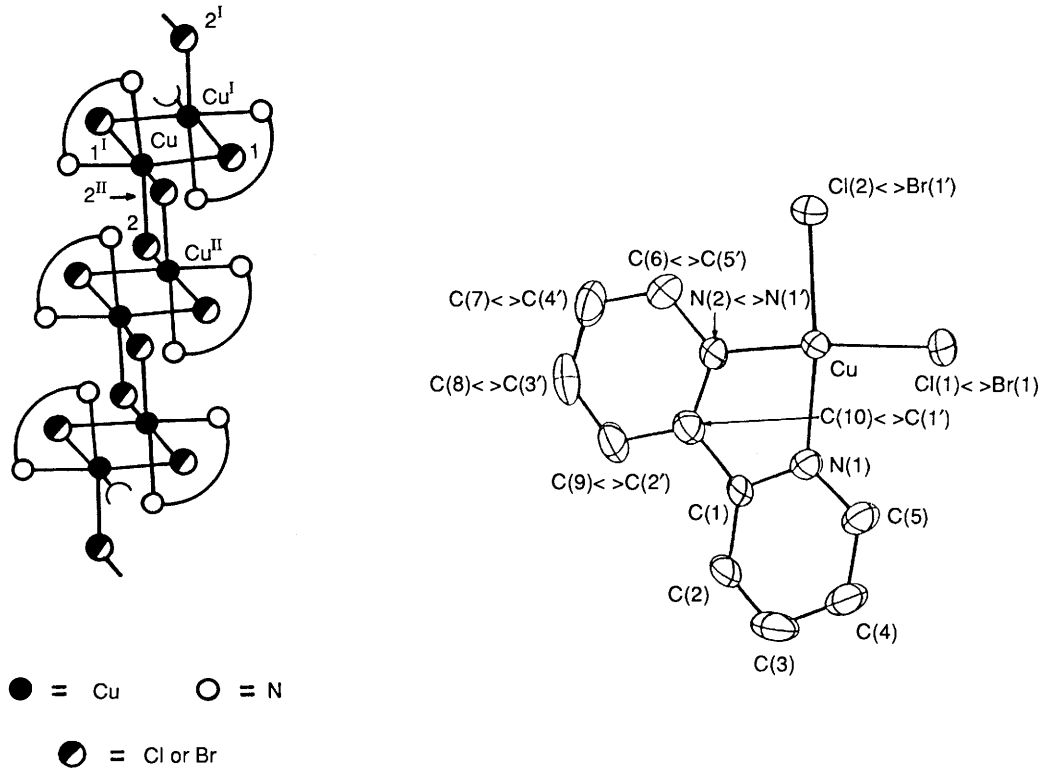

Fig. 2 The structure of Cu(bipy)X_2 (X = Br or Cl)

range $10 < T < 50$ K were used for a mean-squares calculation of θ and the Curie constant. The calculated values for $Cu(bipy)Cl_2$ are $C = 0.39$ and $\theta = -2.3$ K, and for $Cu(bipy)Br_2$, $C = 0.40$ and $\theta = -2.7$ K. The low negative values of θ are indicative of a weak antiferromagnetic interaction. The magnetic susceptibility data do not exhibit a maximum in the studied temperature range. However, polymeric alternating compounds such as dichloro(3,6-dithiaoctane)-copper(II), $Cu(dto)Cl_2$, and lithium copper(II) trichloride dihydrate, $LiCuCl_3 \cdot 2H_2O$, have a magnetic susceptibility maximum at 4.2 and 6.6 K, indicative of antiferromagnetic interactions.[16] The first mentioned complex has alternating sulphur and chlorine bridges, while the second has halogen bridges. The studied chloro and bromo complexes have exclusively halogen bridges.

The X-ray results for the chloro and bromo complexes show that the copper(II) ions are alternately spaced along the crystallographic X axis and along the Z axis respectively, with essentially no interaction between chains (Fig. 2). Therefore they can be considered as one-dimensional polymers.

The Heisenberg alternating-chain theory, as expected in view of the structure of the compound, should provide an accurate description of the temperature dependence of the magnetic susceptibility. An appropriate Hamiltonian for such a system may be written as in equation (1), where J is the exchange

$$H = -2J \sum_{i=1}^{n/2} |\hat{S}_{2i}\hat{S}_{2i-1} + \alpha \hat{S}_{2i}\hat{S}_{2i+1}| \qquad (1)$$

integral between a spin and one of its nearest neighbours and αJ is the exchange integral of the same spin with the other nearest neighbour in the chain. The alternation parameter, α, is temperature independent. The model reproduces the dimeric case for $\alpha = 0$ and the uniform Heisenberg chain for $\alpha = 1$. Duffy and Barr[18] have investigated solutions of the Hamiltonian (1) for the alternating chain, when $0 < \alpha < 1$. Hatfield and coworkers[13,14] have repeated the calculations for this model system and obtained numerical data for the generation of the magnetic susceptibility in terms of the exchange coupling constant J and the alternation parameter α [equation (2)],

$$\chi_R = \frac{AT_R^2 + BT_R + C}{T_R^3 + DT_R^2 + ET_R + F} \qquad (2)$$

where $\chi_R = \chi|J|/Ng^2\mu_B^2$ and the reduced temperature T_R is given by $kT/|J|$. The constants A–F are power series in α. The constant A was set equal to 0.25 for convergence to the Curie law at high temperatures.

Equation (2) was used to fit the experimental data for the chloro and bromo complexes. The best fit was obtained with a fixed value of $g = 2.1$, and the calculated parameters were $J = -0.83$ cm^{-1} and $\alpha = 0.22$ for the chloro complex and $J = -1.00$ cm^{-1} and $\alpha = 0.26$ for the bromo complex. These results are to be compared with the values obtained from the analysis made using the Bleaney–Bowers equation (3) for dimeric

$$\chi_M = \frac{2Ng2\mu_B^2}{3k(T-\theta)}[1 + \tfrac{1}{3}\exp(2J/kT)]^{-1} \qquad (3)$$

copper(II) complexes. The function minimized in curve fitting, with use of a non-linear fitting routine, was $F = \Sigma_i(\chi_i^{obs} - \chi_i^{calc})^2/(\chi_i^{obs})^2$. The dimer model gives a fit, which although statistically good, has a correction term, $\theta = -1.82$ and -2.72 K for the chloro and bromo complexes, that is greater than the corresponding calculated J values (-0.62 and -0.44 cm^{-1} for the chloro and bromo complexes respectively). In this case the physical meaning of the calculated parameters is not clear.

Table 1 summarizes the important bond distances and angles of the complexes. If one compares the values for $Cu(bipy)Cl_2$ and $Cu(dto)Cl_2$ the following remarks can be made. For the 2,2′-bipyridine complex the copper–copper distance in one Cu_2Cl_2 planar unit is 3.802(1) and in the second 3.876(1) Å. For $Cu(dto)Cl_2$ the copper–copper distance in the Cu_2Cl_2 planar unit is 4.406(1) Å, and in the Cu_2S_2 planar unit the separation is 4.679(1) Å. The copper atoms zigzag down the chain with a Cu′–Cu–Cu″ angle of 127.6(1)° in this complex, while the same angle has a less acute value of 143.32(2)° in $Cu(bipy)Cl_2$. The two bridging angles in the $Cu(dto)Cl_2$ complex are

Table 1 Important bond distances (Å) and angles (°) for $Cu(bipy)Cl_2$,[a] $LiCuCl_3 \cdot 2H_2O$[b] and $Cu(dto)Cl_2$[c]

Compound						
	$Cu \cdots Cu^{II}$	$Cu \cdots Cu^{I}$	Cu–Cl(2)	$Cu \cdots Cl(2^{II})$	Cu–Cl(1)	$Cu \cdots Cl(1^{I})$
$Cu(bipy)Cl_2$	3.802(1)	3.876(1)	2.267(1)	3.106(1)	2.267(1)	3.035(1)
	Intradimer	Interdimer	Intradimer	Intradimer	Interdimer	Interdimer
	Cu···Cu	Cu···Cu	Cu–Cl	Cu–Cl	Cu–Cl	Cu–Cl
$LiCuCl_3 \cdot 2H_2O$	3.399	3.820	2.301	2.307	2.258	2.922
	Intradimer	Interdimer	Intradimer	Intradimer	Interdimer	Interdimer
	$Cu \cdots Cu(Cu_2Cl_2)$	$Cu \cdots Cu(Cu_2S_2)$	Cu–Cl	Cu···Cl	Cu–S	Cu···S
$Cu(dto)Cl_2$	4.406(1)	4.679(1)	2.264(1)	3.234(1)	2.327(1)	3.361(2)
	$Cu–Cl(2^{II})–Cu^{II}$	$Cu–Cl(1^{I})–Cu^{I}$	Cl(1)–Cu–Cl(2)	Cl(2)–Cu–$Cl(2^{II})$	$Cu^{I}–Cu–Cu^{II}$	
$Cu(bipy)Cl_2$	90.82	90.58	92.71	89.05	143.3	
	Intradimer	Interdimer	Monomer	Dimer	Polymer chain	
	Cu–Cl–Cu	Cu–Cl–Cu	Cl–Cu–Cl	Cu–Cl–Cu	Cu–Cu–Cu	
$LiCuCl_3 \cdot 2H_2O$	95.08	94.25	—	—	—	
	Intradimer	Interdimer	Monomer	Dimer	Polymer chain	
	Cu–Cl–Cu	Cu–S–Cu	Cl–Cu–Cl	Cl–Cu–Cl	Cu–Cu–Cu	
$Cu(dto)Cl_2$	93.1	109.3	99.4	86.9	127.6	

[a] The superscripts correspond to atoms of neighbouring monomeric units (see Fig. 2). Ref. 20. [b] Ref. 21. [c] Ref. 16.

Table 2 Magnetic parameters for chloro or bromo compounds with alternating-chain magnetism

Compound	Model	$-J/cm^{-1}$	α	g	$-\theta/K$	Ref.
$Cu(mim)_2Br_2$	Heisenberg	7.2	0.40	2.14	—	14
$Cu(4Me\text{-}py)_2Cl_2$	Heisenberg	9.6	0.67	2.17	—	14
$Cu(dto)Cl_2$	Heisenberg	2.73	0.69	2.084	—	16
$LiCuCl_3 \cdot 2H_2O$	Heisenberg	3.7	0.89	2.14	—	16
$Cu(bipy)Br_2$	Heisenberg	1.0	0.26	2.1	—	This work
$Cu(bipy)Cl_2$	Heisenberg	0.83	0.22	2.1	—	This work
$Cu(bipy)Br_2$	Bleaney–Bowers	0.44	0	2.09	2.72	This work
$Cu(bipy)Cl_2$	Bleaney–Bowers	0.62	0	2.06	1.82	This work

are Cu–Cl(2′)–Cu′ and Cu–S(2″)–Cu″, with values of 93.1(1) and 109.3(1)° respectively. The corresponding angles in the $Cu(bipy)Cl_2$ complex are Cu–Cl(2)–Cu^{II} and Cu–Cl(1)–Cu^{I} with values of 90.82(3) and 90.58(3)°.

Considering the lack of structurally and magnetically characterized complexes with an alternating chain bridged by halogen atoms at room temperature, it is impossible to make a good analysis. The only possibility is to compare with compounds that show a magnetic behaviour corresponding to alternating chains. The complexes $Cu(4Me\text{-}py)_2Cl_2$ (4Me-py = 4-methylpyridine) and $Cu(mim)_2Br_2$ (mim = *N*-methylimidazole) have uniform chain structures at room temperature, but their low-temperature magnetic susceptibilities are explained by the alternating-chain theory.[14] The data shown in Table 2 correspond to halide-bridged complexes with antiferromagnetic interactions.

Most data for halide-bridged copper(II) dimers and polymers reveal that the exchange coupling constant is a function of the angle at the ligand bridge (φ) and the length of the superexchange path way (R_0). Correlations have been made for J with the quotient φ/R_0 for chloro- and bromo-bridged copper(II) complexes.[5] The values of φ/R_0 for $Cu(dto)Cl_2$ are 28.8 and 32.5° $Å^{-1}$ for the planar Cu_2Cl_2 and Cu_2S_2 units and 32.2° $Å^{-1}$ for $LiCuCl_3 \cdot 2H_2O$. These values suggest that antiferromagnetic behaviour should be observed.[5] This is confirmed by the maximum in the susceptibility curve at 4.2 K for $Cu(dto)Cl_2$, with a calculated value of $J = -2.73\ cm^{-1}$, and a maximum at 6.6 K for $LiCuCl_3 \cdot 2H_2O$, with a calculated value of $J = -3.7\ cm^{-1}$. However, the experimental value of J is lower than the predicted value. The magnitudes of φ/R_0 for $Cu(bipy)Cl_2$ are of the same order, 29.8 and 29.2° $Å^{-1}$ for the two planar Cu_2Cl_2 units. However the calculated J value is near zero, $-0.83\ cm^{-1}$. The bromo complex has a similar value of the magnetic exchange parameter, $J = -1.00\ cm^{-1}$. This behaviour is observed frequently in chloro and bromo compounds.[22] Thus it is not possible to estimate the exact magnitude of the exchange coupling constant from structural data alone. There must be an electronic factor that is influencing the exchange interaction. The presence of sulphur bridges has been cited as very effective in transmitting superexchange interactions.[23,24] However, if one compares the data given for $Cu(dto)Cl_2$ and for $LiCuCl_3 \cdot 2H_2O$, the complex with sulphur bridges has a lower value of J than the complex with exclusive halogen bridges. Besides, the studied chloro complex, $Cu(bipy)Cl_2$, does not present a maximum in the same range of the susceptibility curve (4–7 K).

It is evident that more work has to be done on alternating copper(II) polymers to obtain a better understanding of the factors that govern the magnetic behaviour of these compounds.

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