A Study of the Magnetic Properties of Copper(II) Pyrazinamide Complexes

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The magnetic susceptibilities of the compounds [Cu(pyzA)$_2$Cl$_2$], [Cu(pyzA)$_2$Br$_2$], and [{Cu(pyzA)$_2$(ClO$_4$)$_2$}$_n$] (where pyzA = pyrazine-2-carboxamide) were measured between 1·7 and 280 K. The perchlorate complex exhibits Curie–Weiss behaviour to low temperatures. The susceptibilities of the halide complexes maximize at 17 K for the chloride and at *ca.* 31 K for the bromide. The experimental results are described by the Heisenberg model for a one-dimensional chain exhibiting antiferromagnetic interactions. Consistent with i.r. observations reported previous to this work, the observed susceptibilities of the halide complexes are indicative of a halogen-bridged infinite-chain structure for these species.

COPPER(II) complexes of pyrazine-2-carboxamide (hereafter referred to as pyrazinamide, pyzA) were initially reported by Sekizaki and Yamasaki.[1] There are many structures that can be proposed for copper(II)–pyrazinamide complex compounds because this potentially multidentate ligand can interact with a metal ion in several ways. Based upon the normal room temperature magnetic moments and the i.r. spectra of these complexes, Sekizaki and Yamasaki proposed square-planar monomeric structures for the complexes [Cu(pyzA)$_2$Cl$_2$], [Cu(pyzA)$_2$Br$_2$], and [{Cu(pyzA)$_2$(ClO$_4$)$_2$}$_n$].

A subsequent crystal-structure determination[2] of [{Cu(pyzA)$_2$(ClO$_4$)$_2$}$_n$] revealed that the copper ions of this complex are actually six-co-ordinate and are linked together through the pyrazinamide ligands to form an infinite two-dimensional polymeric molecular framework. In the perchlorate complex, pyrazinamide is tridentate, bonding to one copper atom through the carbonyl oxygen of the amide group and the aromatic nitrogen *ortho* to the amide function, while weakly interacting with a neighbouring copper ion through the ring nitrogen atom *meta* to the carboxamide moiety.

A large number of copper complexes of the type [CuL$_2$X$_2$] (where L is an aromatic nitrogen-containing ligand and X is a halogen) are known and some have been structurally characterized. The molecular structures of the parent complexes of this series, [Cu(pyridine)$_2$Cl$_2$] and [Cu(pyridine)$_2$Br$_2$], have been determined to be halide-bridged one dimensional polymers.[3,4] The structures of the related compounds [Cu(4-vinylpyridine)$_2$Cl$_2$][5] and [Cu(4-ethylpyridine)$_2$Cl$_2$][6] have been shown to possess structures analogous to the copper halide–pyridine compounds. By way of contrast, [Cu(2-picoline)$_2$Cl$_2$] and [Cu(2-picoline)$_2$Br$_2$] are halogen-bridged dimers.[7,8]

In addition to these known structures, the magnetic properties of some [CuL$_2$X$_2$] complexes are indicative of polymeric structures. For example, chloride-bridged chain structures have been proposed for [Cu(2,6-dimethylpyrazine)$_2$Cl$_2$][9] and [Cu(2-methylquinoxaline)$_2$Cl$_2$][10] on the basis of low-temperature magnetic susceptibility studies of those compounds.

Copper(II) is known to have a tendency to form distorted octahedral complexes.[11] Given this tendency, plus the ability of pyrazine to form polymeric complexes with copper(II) by interaction with metal ions at both aromatic nitrogen atoms,[2,12] the square-planar monomeric structures originally suggested[1] for [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$] seem rather unlikely. It is more probable that these complexes are polymeric, like [{Cu(pyzA)$_2$(ClO$_4$)$_2$}$_n$] and the related compounds described above. Since novel magnetic behaviour is often associated with polymeric transition-metal complexes, and since the magnetic behaviour of these kinds of compounds affords a good clue as to the nature of their structures, a detailed study of the low-temperature magnetic properties of [Cu(pyzA)$_2$Cl$_2$], [Cu(pyzA)$_2$Br$_2$], and [{Cu(pyzA)$_2$(ClO$_4$)$_2$}$_n$] was undertaken.

EXPERIMENTAL

Blue crystals of [{Cu(pyzA)$_2$(ClO$_4$)$_2$}$_n$] were obtained by the method of Sekizaki.[2] The crystals were slightly hygroscopic but were stable at room temperature over anhydrous CaCl$_2$ in a desiccator (Found: C, 23·5; H, 1·9; N, 16·3. Calc. for $CuC_{10}H_{10}N_6Cl_2O_{10}$: C, 23·61; H, 1·98; N, 16·52%). Stable fluffy powders of green [Cu(pyzA)$_2$Cl$_2$] and golden [Cu(pyzA)$_2$Br$_2$] precipitated immediately upon mixing stoicheiometric amounts of aqueous solutions of the appropriate copper halide and of pyrazinamide (Found: C, 31·85; H, 2·7; N, 21·85. Calc. for $CuC_{10}H_{10}N_6Cl_2O_2$: C, 31·55; H, 2·65; N, 22·08%. Found: C, 25·4; H, 2·2; N, 17·7. Calc. for $CuC_{10}H_{10}N_6Br_2O_2$: C, 25·57; H, 2·15; N, 17·90%).

Magnetic susceptibility measurements were determined in the temperature range 1·7 to 280 K using a P.A.R.

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Foner-type vibrating sample magnetometer[13] calibrated with mercury tetrathiocyanatocobaltate(II).[14] All susceptibility measurements were made at a field strength of 10 000 G. Temperatures were measured with a calibrated gallium arsenide diode. Susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constants[15] and for TIP[16] (according to $N\Delta g\beta^2/\lambda$). Electron paramagnetic resonance spectra were recorded on a Varian model E-2 spectrometer at X band using DPPH as an internal standard. I.r. spectra were obtained from a Perkin-Elmer model 421 recording spectrometer.

RESULTS AND DISCUSSION

Magnetic susceptibility measurements of a polycrystalline sample of $[Cu(pyzA)_2(ClO_4)_2]$ between 1·7 and 280 K show no direct evidence of magnetic exchange in the polymer. The Curie–Weiss behaviour of the experimental inverse susceptibility is illustrated in Figure 1. These results can be described by the Curie–Weiss Law[17]

$$\chi_m = C/(T - \theta) \qquad (1)$$

where

$$C = Ng^2\beta^2S(S + 1)/3k \qquad (2)$$

from 10 to 280 K with $S = 1/2$, $g = 2{\cdot}18$, and $\theta = -1{\cdot}9°$. Below 10 K, there is a small positive deviation from Curie–Weiss behaviour which, along with the negative Weiss constant, may be indicative of weak long-range ferromagnetic interactions. Direct evidence of such a phenomenon might be observable at temperatures below 1·7 K, the low limit of this experiment.

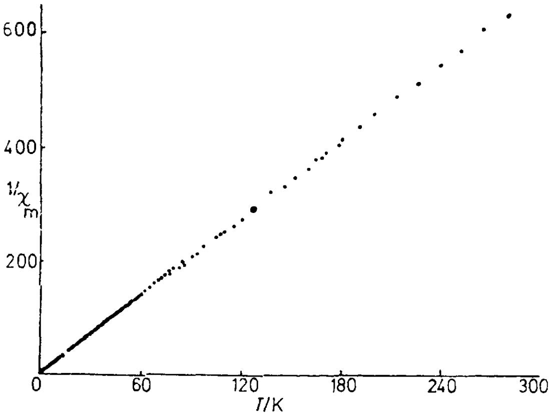

FIGURE 1 Inverse magnetic susceptibility (c.g.s. units) *vs.* temperature of $[Cu(pyzA)_2(ClO_4)_2]$. Experimental points are indicated as solid circles

The e.p.r. spectrum of a powdered specimen of $[\{Cu(pyzA)_2(ClO_4)_2\}_n]$ at 77 K displayed three g values at $g = 2{\cdot}14$, 2·16, and 2·21. The average g of 2·17 is in excellent agreement with the average g value obtained from the Curie–Weiss fit of the susceptibility results.

The experimental magnetic susceptibility *versus* temperature results for the complexes $[Cu(pyzA)_2Cl_2]$ and $[Cu(pyzA)_2Br_2]$ are shown in Figures 2 and 3, respectively. The chloride data exhibit a susceptibility maximum at 17 K, while the bromide complex displays the same effect at *ca.* 31 K. It is presumed that, owing to the rapid precipitation of these water-insoluble halide complexes inherent in their syntheses, significant amounts of paramagnetic impurities are unavoidably trapped in the samples and this accounts for the rise in the measured moment recorded for the halide compounds at very low temperatures.

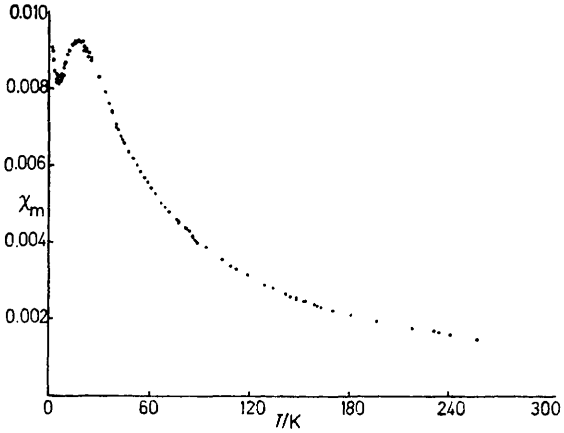

FIGURE 2 Molar magnetic susceptibility in c.g.s.u. *vs.* temperature of $[Cu(pyzA)_2Cl_2]$

Because the structures of the halide complexes have not been determined, attempts were made to describe the magnetic data with model expressions which could account for the gross features of the experimental results. Because the structures of $[\{Cu(2\text{-picoline})_2Cl_2\}_2]$ and $[\{Cu(2\text{-picoline})_2Br_2\}_2]$ are dimeric,[7,8] attempts were made to describe the copper pyrazinamide halide magnetic data in terms of the Bleaney–Bowers equation

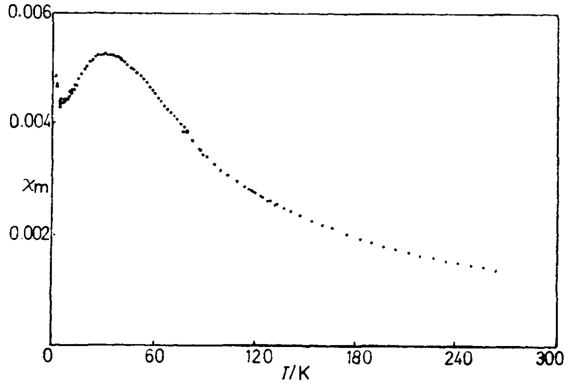

FIGURE 3 Molar magnetic susceptibility in c.g.s.u. *vs.* temperature of $[Cu(pyzA)_2Br_2]$

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for exchange-coupled $S = 1/2$ dimers.[18] These attempts were unsuccessful for any reasonable values of exchange parameters, and this is taken to be evidence that [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$] are not dimeric compounds.

The probability of polymeric structures for [Cu(pyzA)$_2$-Cl$_2$] and [Cu(pyzA)$_2$Br$_2$] mentioned previously, plus the similarity between the observed magnetic behaviour of these pyrazinamide complexes and that reported [19] for dichlorobis(pyridine)copper(II) and dibromobis(pyridine)-copper(II), and for dichlorobis(4-ethylpyridine)copper(II), and dichlorobis(4-vinylpyridine)copper(II),[20] all of which are halide-bridged chains,[3-6] suggested that the magnetic properties of [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$] may be explained in terms of chain structures.

The Hamiltonian for spin interaction between neighbouring paramagnetic ions in an infinite one-dimensional network is given by [21]

$$H = -J\sum_{i=1}[S_{iz}\cdot S_{(i+1)z} + \gamma(S_{ix}\cdot S_{(i+1)x} + S_{iy}\cdot S_{(i+1)y})] \quad (3)$$

where J is the exchange energy and γ can have values ranging from zero to one. For the limit $\gamma = 1$, the isotropic Heisenberg model is the result, while for $\gamma = 0$ the anisotropic Ising model obtains. Only for the latter case are closed-form expressions available for the magnetic susceptibility of a linear chain of $S = 1/2$ ions.[22] The Heisenberg model can be approximated by using the results of Bonner and Fisher [21] for infinite chains where $kT_{\max}/|J| \approx 1{\cdot}282$ and $|J|\chi_{\max}/g^2\beta^2N \approx 0{\cdot}0735$. Although the anisotropic model, because of the ease with which experimental data may be described by the Ising closed-form expressions, is an attractive one to use in these cases, Jotham [23] has pointed out (with reference to dimeric copper dicarboxylates) serious deficiencies inherent in the use of the anisotropic simplification of the spin Hamiltonian (3). Furthermore, g values obtained as parameters from Ising descriptions of the magnetic properties of the [Cu(pyrazinamide)$_2$X$_2$] complexes are not in good agreement with the average g values recorded for these compounds from powder e.p.r. spectra. The Heisenberg approximation was therefore chosen to describe the magnetic properties of [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$].

The best fits obtained for the [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$] magnetic data from the Heisenberg isotropic linear model are shown in Figure 4.

The magnetic data was corrected for the inclusion of paramagnetic impurities by assuming that the observed molar susceptibilities were the sum of the susceptibility of the paramagnetic impurity plus the susceptibility arising from the linear chain. By assuming that all paramagnetic contributions to the total susceptibility obeyed the Curie Law, the following expression for the total susceptibility resulted:

$$\chi_{\text{total}} = (p[Ng^2\beta^2S(S+1)]/3kT) + (1{\cdot}0 - p)\chi_{\text{Heisenberg}} \quad (4)$$

where $p = \%$ impurities/100, $S = 1/2$, and where g was set equal to average e.p.r.-recorded g values of the respective complexes. (Owing to the small magnitudes of p, χ_{total} is insensitive to minor changes of the g value used in the correction term.) A 1·2% impurity correction was applied to the chloride data, and a 0·5% correction added to the bromide results. The parameters obtained for [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$] along with Heisenberg results reported for other linear chain antiferromagnetic [CuL$_2$X$_2$] complexes are compared in the Table. It is estimated that the J values are accurate to $\pm 1{\cdot}0$ cm^{-1} and the $\langle g\rangle$ values to $\pm 0{\cdot}005$.

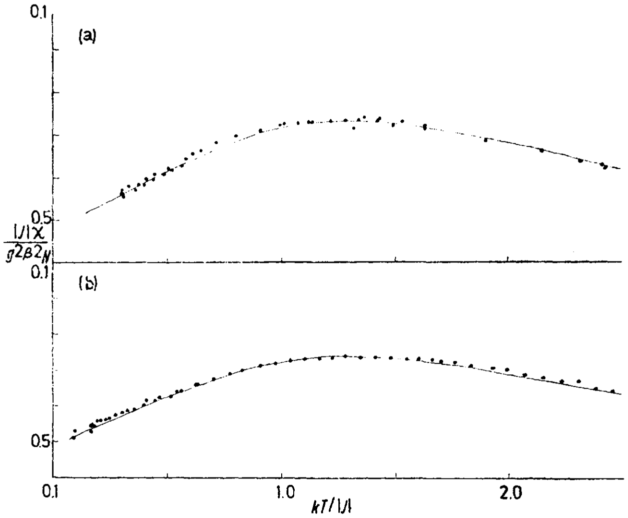

FIGURE 4 (a) Temperature variation of the reduced susceptibility of [Cu(pyzA)$_2$Cl$_2$] plotted along with the curve of the estimated limit for infinite Heisenberg chains. (b) Heisenberg fit for [Cu(pyzA)$_2$Br$_2$]

E.p.r. spectra of the halide pyrazinamide complexes were determined at 77 K for powdered samples. The spectrum obtained from the chloride displayed three g values at 2·25, 2·06, and 2·04 ($\langle g\rangle = 2{\cdot}12$), while the bromide spectrum showed one broad absorption centred at $g = 2{\cdot}11$. No fine structure was observed in either sample. The good agreement of the g values calculated as a Heisenberg model parameter with these experimentally determined results illustrates the validity of the Heisenberg isotropic linear-chain approximation for describing the magnetism of [Cu(pyzA)$_2$Cl$_2$] and [Cu(pyzA)$_2$Br$_2$].

The i.r. spectra obtained for the three complexes studied, plus that of the free pyrazinamide ligand, are identical to the results reported [1] by Sekizaki and Yamasaki, and

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support their conclusion that pyrazinamide is bonded to copper in [$Cu(pyzA)_2Cl_2$] and [$Cu(pyzA)_2Br_2$] solely by the aromatic nitrogen atom ***meta*** to the carboxamide group. If this be the case, the pyrazinamide ligands can be regarded [insofar as the manner in which they are bonded to the copper(II) ion] as being analogous to the pyridine and substituted pyridine ligands of the complexes [$Cu(pyridine)_2Cl_2$], [$Cu(pyridine)_2Br_2$], [$Cu(4$-vinylpyridine$)_2Cl_2$], and [$Cu(4$-ethylpyridine$)_2Cl_2$]. The marked similarities of the magnetic properties of all structures are all analogous halide-bridged chains. The postulated structure of [$Cu(pyzA)_2Cl_2$] and [$Cu(pyzA)_2Br_2$] is illustrated in Figure 5.

Some structural parameters determined for antiferromagnetically coupled halide-bridged linear chain [CuL_2X_2] complexes are presented in the Table. The striking similarities of all these structures is evidence that the mechanism of exchange interaction through the copper halide chains of these complexes is the same. Because the exchange parameters determined for these complexes, coupled with the infrared evidence of no bonding interaction between copper(II) ions and the carboxamide group of pyrazinamide in [$Cu(pyzA)_2Cl_2$] and [$Cu(pyzA)_2Br_2$] lead to the conclusion that their [$Cu(pyzA)_2Cl_2$] and [$Cu(pyzA)_2Br_2$] are similar to those deduced for the four complexes above, it is reasonable to infer the same exchange mechanism for the copper pyrazinamide halides. Therefore it is predicted that the Cu–X–Cu angles along the copper–halogen chains of the [$Cu(pyzA)_2X_2$] complexes are near 90°.

Magnetic and structural data for some linear-chain copper(II) complexes

	J/cm^{-1}	$\langle g \rangle$	Cu–Cu separation, Å	Cu–X–Cu bridge angle	Refs.
[$Cu(pyzA)_2Cl_2$]	$-10{\cdot}7$	2·12			This work
[$Cu(pyridine)_2Cl_2$]	$-9{\cdot}15$	2·50	3·87	92°	3, 19
[$Cu(pyzA)_2Br_2$]	$-16{\cdot}6$	2·125			This work
[$Cu(pyridine)_2Br_2$]	$-18{\cdot}9$	2·11	4·04	93°	4, 19
[$Cu(4$-vinylpyridine$)_2Cl_2$]	$-7{\cdot}8$	2·03	4·04	90°	5, 20
[$Cu(4$-ethylpyridine$)_2Cl_2$]	$-6{\cdot}7$	2·10	4·00	92°	6, 20

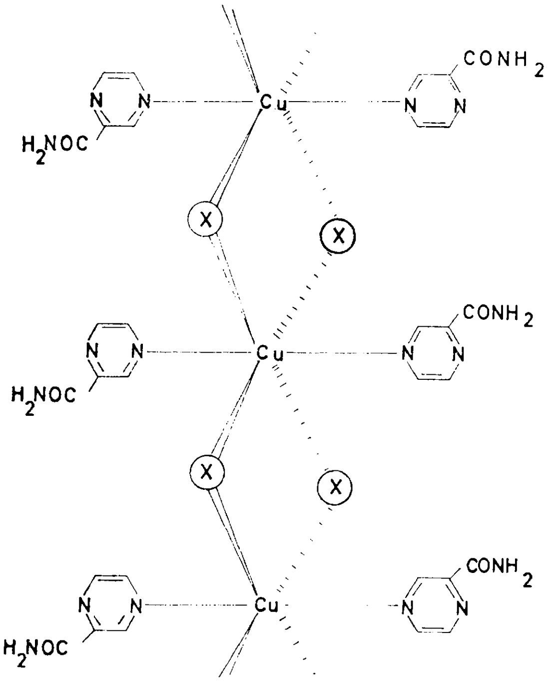

FIGURE 5 Proposed structure of dihalogenobis(pyrazinamide)-copper(II). X = Cl or Br. (The use of 'hatched' bonds between copper and X does not imply that these bonds are elongated. The usual *trans*-elongated octahedral stereochemistry probably obtains for these compounds)

It has been shown [24] that antiferromagnetic exchange results when two d^9 cations interact through a single orbital of a bridging anion even when the bridging cation–anion–cation angle is 90°. Such a mechanism is consistent with the observed magnetism of [$Cu(pyzA)_2Cl_2$] and [$Cu(pyzA)_2Br_2$] and with the structures proposed here for these complexes.

It is of interest to compare the magnetic properties of [$\{Cu(pyzA)_2(ClO_4)_2\}_n$] to those of the series [$\{Cu($substituted-pyrazine$)(NO_3)_2\}_n$], which have pyrazine-bridged linear-chain structures. The substituted pyrazine complexes exhibit antiferromagnetic linear chain magnetism with the magnetic parameters: [25-28]

	$2J$/cm^{-1}	$\langle g \rangle$
[$\{Cu(quinoxaline)(NO_3)_2\}_n$]	$-9{\cdot}0$	2·15
[$\{Cu(pyrazine)(NO_3)_2\}_n$]	$-7{\cdot}2$	2·133
[$\{Cu(methylpyrazine)(NO_3)_2\}_n$]	$-6{\cdot}2$	2·145
[$\{Cu(chloropyrazine)(NO_3)_2\}_n$]	$-2{\cdot}8$	2·153

It has been proposed [27] that the spin-exchange mechanism for the pyrazine complexes involves the coupling of the electrons in the $\sigma^*(d_{x^2-y^2})$ orbitals on copper through the highest-energy occupied molecular-orbital on the pyrazine bridge. Since the pyrazine ring is canted with respect to the xy-plane of copper,[12] this orbital has the proper symmetry to overlap with the σ^* copper orbital. An examination of the structural features of [$\{Cu(pyzA)_2(ClO_4)_2\}_n$] quickly shows that an analogous mechanism for

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spin–spin coupling through the pyrazinamide bridge is not possible. The structure [2] of $[\{Cu(pyzA)_2(ClO_4)_2\}_n]$ consists of two *trans*-co-ordinated ligands utilizing pyrazine nitrogen and amide oxygen donor atoms. Tetragonally distorted octahedral co-ordination about copper, and the formation of a two-dimensional network, is achieved by co-ordination of nitrogen-4 from pyrazines in two neighbouring units. These out-of-plane Cu–N bond distances are 2·485 Å. The π-orbitals of the ring in pyrazinamide are orthogonal both to the σ^* orbital of the copper ion to which the ligand is tightly bonded, and to the σ^* orbital of the copper to which the nitrogen-4 atom is bonded. Thus, only 'potential' exchange [29] is possible and any coupling would be expected to be of ferromagnetic nature. This prediction is in agreement with the negative Weiss constant which was observed.

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