Magnetic Properties of Polymeric Dihalogenodi(nicotinamide)- and Dihalogenodi(isonicotinamide)-copper(II) Complexes

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Magnetic susceptibilities of powdered samples of complexes of the general formula $[\{\mathrm{CuL_2X_2}\}_n]$ (X = Cl or Br, L = nicotinamide or isonicotinamide) have been determined in the temperature range 4·2—286 K. The data reflect an antiferromagnetic interaction of the linear-chain type and suggest a common structural assignment for all four complexes. The structures are expected to be di-μ-halogeno-bridged chains analogous to those of $[\{\mathrm{Cu(py)_2X_2}\}_n]$ (X = Cl and Br, py = pyridine).

MAGNETIC[1] and spectral[1,2] studies of the copper(II) halide complexes of pyrazine-2-carboxamide have led to the conclusion that $[\{\mathrm{Cu(pyzc)_2Cl_2}\}_n]$ and $[\{\mathrm{Cu(pyzc)_2Br_2}\}_n]$ (pyzc = pyrazine-2-carboxamide) are made up of infinite chains of six-co-ordinate copper(II) ions joined by halide bridges. Similar investigations of copper(II) halide complexes of the related ligand pyridine-2-carboxamide have shown that they are monomeric, having tetragonally distorted octahedral co-ordination about each copper ion.[3,4]

Bivalent transition-metal chloride complexes of the remaining pyridine-carboxamide ligands, pyridine-3-carboxamide (nicotinamide, na) and pyridine-4-carboxamide (isonicotinamide, ina), have been reported,[2,5,6] and i.r. spectral studies indicated that the carboxamide groups of these ligands do not co-ordinate to the metal ions. These i.r. characteristics are quite similar to those of the complexes $[\{\mathrm{Cu(pyzc)_2Cl_2}\}_n]$ and $[\{\mathrm{Cu(pyzc)_2Br_2}\}_n]$ which suggest that $[\{\mathrm{Cu(na)_2X_2}\}_n]$ and $[\{\mathrm{Cu(ina)_2X_2}\}_n]$ (X = Cl or Br) may show evidence of antiferromagnetic exchange interaction at low temperatures, analogous to the behaviour exhibited by the pyzc complexes. Accordingly, as part of a study of polymeric complexes of the general type $[\{\mathrm{CuL_2X_2}\}_n]$ (L = an aromatic nitrogen-containing ligand), the complexes $[\{\mathrm{Cu(na)_2Cl_2}\}_n]$, $[\{\mathrm{Cu(na)_2Br_2}\}_n]$, $[\{\mathrm{Cu(ina)_2Cl_2}\}_n]$, and $[\{\mathrm{Cu(ina)_2Br_2}\}_n]$ were

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prepared by known methods and their magnetic and i.r. properties studied to determine the nature and extent of any magnetic exchange present.

EXPERIMENTAL

The method of Nagano [5] was used to prepare all four complexes. To an ethanolic solution of nicotinamide (na) or isonicotinamide (ina) was added stoicheiometric amounts of ethanolic solutions of $CuCl_2 \cdot 2H_2O$ or $CuBr_2$. Insoluble precipitates of $[\{Cu(na)_2Cl_2\}_n]$, $[\{Cu(na)_2Br_2\}_n]$, $[\{Cu(ina)_2Br_2\}_n]$, and $[\{Cu(ina)_2Cl_2\}_n]$ immediately formed. These were removed from solution by filtration, washed with ethanol, acetone, and diethyl ether, and dried for 6 h *in vacuo* at 50 °C. Both chloride complexes were light blue crumbly powders, while the two bromide complexes were yellow-green resembling the chloride species in texture. All four complexes were insoluble in water, acetone, diethyl ether, methanol, and ethanol and sparingly soluble in *NN*-dimethylformamide, dimethyl sulphoxide, and acetonitrile [Found: C, 37·85; H, 3·45; N, 14·9. Calc. for $Cu(na)_2Cl_2$, $CuC_{12}H_{12}N_4O_2Cl_2$: C, 38·05; H, 3·20; N, 14·8. Found: C, 37·85; H, 2·95; N, 14·8. Calc. for $Cu(ina)_2Cl_2$, $CuC_{12}H_{12}N_4O_2Cl_2$: C, 38·05; H, 3·20; N, 14·8. Found: C, 30·45; H, 2·45; N, 11·6. Calc. for $Cu(na)_2Br_2$, $CuC_{12}H_{12}N_4O_2Br_2$: C, 30·8; H, 2·60; N, 12·0. Found: C, 30·35; H, 2·40; N, 11·6. Calc. for $Cu(ina)_2Br_2$, $CuC_{12}H_{12}N_4O_2$: C, 30·82; H, 2·60; N, 12·0%]. Microanalyses were by P.C.R. Inc., Gainesville, Florida.

Magnetic-susceptibility measurements over the complete temperature range of 1·7—286 K on powder samples of $[\{Cu(ina)_2Cl_2\}_n]$, $[\{Cu(ina)_2Br_2\}_n]$, and $[\{Cu(na)_2Br_2\}_n]$ were recorded with a Foner-type vibrating-sample magnetometer [7] at a field strength of 10 000 G provided by an electromagnet controlled by a Ventron–Magnion precision power supply. The same system was utilized to obtain susceptibility data for $[\{Cu(na)_2Cl_2\}_n]$ in the temperature range 77—285 K. Low-temperature (4·2—77 K) results for $[\{Cu(na)_2Cl_2\}_n]$ were obtained from the vibrating-sample magnetometer, employing a measuring field of *ca.* 10 022 G supplied by a P.A.R. model 150-A superconducting magnet. Temperatures were measured with a calibrated gallium arsenide diode. The magnetometer was calibrated with mercury(II) tetrathiocyanatocobaltate(II).[8,9] In general, the magnetic susceptibilities are accurate to $\pm 1\%$. All susceptibility measurements were corrected for the diamagnetism of constituent atoms using Pascal's constants,[10] and for temperature-independent paramagnetism (t.i.p.) [11] (according to $N\Delta g\beta^2/\lambda = 60 \times 10^{-6}$ c.g.s. units). E.p.r. spectra of powder samples were recorded at *X*-band at 77 K on a Varian model E-3 spectrometer using diphenylpicrylhydrazine as an internal standard. I.r. spectra of solid KBr pellet specimens were recorded on a Perkin-Elmer model 421 recording spectrometer calibrated by an I.U.P.A.C.-certified polystyrene standard.

RESULTS AND DISCUSSION

The experimental magnetic-susceptibility data of polycrystalline samples of $[\{Cu(na)_2Cl_2\}_n]$ and $[\{Cu(na)_2Br_2\}_n]$ are shown in Figure 1. Broad maxima in the susceptibilities of the two complexes are apparent; the susceptibility of $[\{Cu(na)_2Cl_2\}_n]$ maximizes at *ca.* 16 K, while $[\{Cu(na)_2Br_2\}_n]$ exhibits the same effect at *ca.* 38 K. Such behaviour is indicative of antiferromagnetic exchange in these complexes. The rise in the measured moment at the lowest temperatures recorded is due to paramagnetic impurities present in the samples.

There exist a number of complexes of copper(II) possessing $[\{CuL_2X_2\}_n]$ stoicheiometry related to the na complexes. *X*-Ray structural characterizations of the parent complexes of this group, $[\{Cu(py)_2Cl_2\}_n]$ and $[\{Cu(py)_2Br_2\}_n]$ (py = pyridine), have revealed that they are composed of infinite chains of $Cu(py)_2$ groups linked together by di-μ-halogeno-bridges.[12,13] Other structural studies [14,15] have shown analogous structures for the chloro-bridged complexes $[\{Cu(4\text{-vinylpyridine})_2Cl_2\}_n]$ and $[\{Cu(4\text{-Etpy})_2Cl_2\}_n]$. The magnetic susceptibilities of these four complexes have been determined over wide temperature ranges;[16,17] the behaviour that they exhibit is very similar to that observed for $[\{Cu(na)_2Cl_2\}_n]$ and $[\{Cu(na)_2Br_2\}_n]$. If the latter are di-μ-halogeno-chain structures analogous to those described above, the only site of co-ordination to copper(II) ions from the na molecules must be the ring nitrogen atom while the carboxamide moiety does not interact with the metal ions. Accordingly, i.r. spectra of $[\{Cu(na)_2Cl_2\}_n]$, $[\{Cu(na)_2Br_2\}_n]$, and of free na were recorded to determine whether or not the carboxamide group is bonded to the metal ion.

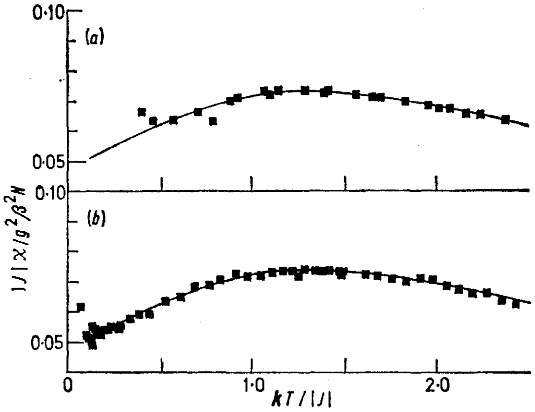

FIGURE 1 Magnetic susceptibilities of $[\{Cu(na)_2X_2\}_n]$ plotted against the reduced temperature: X = Cl (*a*); Br (*b*). Solid lines are best fits to the Heisenberg linear-chain model

Two strong i.r. absorptions at *ca.* 1 700 and 1 400 cm^{-1} are characteristic of the unsubstituted acid amide group,[18] and are diagnostic of carbonyl co-ordination. The two bands of $[\{Cu(na)_2Cl_2\}_n]$ and $[\{Cu(na)_2Br_2\}_n]$ were not substantially shifted away from those of the ligand, which implies that the bonding of na to copper is through the ring nitrogen atom only. The same conclusion was

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reached for the complexes $[\{Cu(pyzc)_2Cl_2\}_n]$ and $[\{Cu(pyzc)_2Br_2\}_n]$.[1] Since the magnetic properties of the pyzc complexes are similar to those determined for those of na, it seemed appropriate that the linear-chain model employed to describe the magnetism of $[\{Cu(pyzc)_2Cl_2\}_n]$ and $[\{Cu(pyzc)_2Br_2\}_n]$ should be utilized to explain that of the corresponding na complexes.

The Hamiltonian for spin interaction between neighbouring paramagnetic ions along an infinite one-dimensional chain is given by equation (1),[19] where J is the

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

exchange energy and γ can have values ranging from 0 to 1. When $\gamma = 1$, the isotropic Heisenberg model is the result, while for the limit $\gamma = 0$ the anisotropic Ising model is obtained. Closed-form expressions for the magnetic susceptibility of a linear chain of ions of $S = \frac{1}{2}$ are available for the Ising model,[20] while the Heisenberg model can be approximated by using the results of Bonner and Fisher[19] for infinite $S = \frac{1}{2}$ chains where $kT_{max.}/|J| = 1{\cdot}282$ and $|J|\chi_{max.}/g^2\beta^2N = 0{\cdot}0735$. The anisotropic Ising simplification of the exchange Hamiltonian (1) is substantially in error for the description of one-dimensional polymeric systems having large exchange interactions.[21] Furthermore, a single-crystal magnetic-susceptibility study[22] of the linear-chain complex $[\{Cu(pyz)_2(NO_3)_2\}_n]$ demonstrated that, even for the small value $|J|/K = 5{\cdot}3°$, the exchange interaction is quite isotropic. The Heisenberg approximation was therefore chosen to describe the experimental magnetic susceptibilities of $[\{Cu(na)_2Cl_2\}_n]$ and $[\{Cu(na)_2Br_2\}_n]$.

Since no closed-form expressions are available for the Heisenberg linear-chain model susceptibility, the experimental data were fitted to the results of Bonner and Fisher[19] graphically. The best fits obtained for the susceptibilities of $[\{Cu(na)_2Cl_2\}_n]$ and $[\{Cu(na)_2Br_2\}_n]$ are shown in Figure 1. The data were corrected for inclusion of paramagnetic impurities which are present due to the rapid precipitation of the complexes during their syntheses. It was assumed that the observed molar magnetic susceptibilities were the sum of the susceptibility of paramagnetic impurities plus that arising from the linear chain.[1] If it is assumed that the susceptibilities of any paramagnetic impurities present obey the Curie law, expression (2) for the total observed magnetic susceptibility results, where p = % impurity/100, $S = \frac{1}{2}$, and g was

$$\chi_T = \{p[Ng^2\beta^2S(S+1)]/3kT\} + (1{\cdot}0 - p)\chi_{chain} \qquad (2)$$

set equal to the value obtained from the Heisenberg fit of the experimental results. A 1·97% impurity correction was incorporated into the Heisenberg fit of the chloride data, and a 0·2% correction was added to the bromide results. The parameters obtained were: for $[\{Cu(na)_2Cl_2\}_n]$, $J = -10{\cdot}1$ cm^{-1} and $g = 2{\cdot}09$; for $[\{Cu(na)_2Br_2\}_n]$, $J = 20{\cdot}6$ cm^{-1} and g 2·14. The J values are estimated to be accurate to $\pm 1{\cdot}0$ cm^{-1}.

The e.p.r. spectrum of $[\{Cu(na)_2Cl_2\}_n]$ showed two absorptions, $g_{\parallel} = 2{\cdot}2$ and $g_{\perp} = 2{\cdot}07$ ($\langle g \rangle$ 2·12). The bromide spectrum consisted of one broad signal centered at $\langle g \rangle = 2{\cdot}11$. These average g values are in reasonable agreement with calculated values of $\langle g \rangle$ obtained from the Heisenberg fits, which illustrates the validity of the isotropic linear-chain model for describing the magnetism of the $[\{Cu(na)_2X_2\}_n]$ complexes.

The experimental magnetic-susceptibility results for $[\{Cu(ina)_2Cl_2\}_n]$ and $[\{Cu(ina)_2Br_2\}_n]$ are shown in Figure 2. Broad maxima in the susceptibilities of both complexes were observed, with $\chi_{max.}$ at 9·5 K for the chloride and 36 K for the bromide species. The usual rise in susceptibility at very low temperatures due to paramagnetic impurities was seen in both cases. These results are very similar to those observed for the corresponding na complexes. The i.r. spectra of ina, $[\{Cu(ina)_2Cl_2\}_n]$, and $[\{Cu(ina)_2Br_2\}_n]$ were recorded over the range 2 000—1 000 cm^{-1}. As was the case for $[\{Cu(na)_2Cl_2\}_n]$ and $[\{Cu(na)_2Br_2\}_n]$, there was no evidence of co-ordination of copper to the carboxamide moiety of ina.

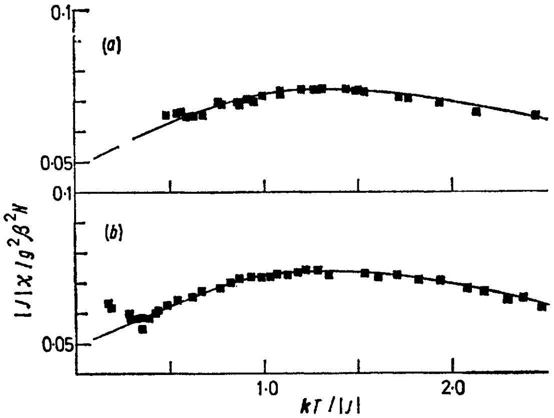

FIGURE 2 Magnetic susceptibilities of $[\{Cu(ina)_2X_2\}_n]$ plotted against the reduced temperature: X = Cl (*a*); Br (*b*). Solid lines as in Figure 1

The data were fitted to the Heisenberg linear-chain approximation in the same manner as described for the na complexes. The results of the best fits are presented in Figure 2. For $[\{Cu(ina)_2Cl_2\}_n]$, $J = -5{\cdot}2$ cm^{-1} and $g = 2{\cdot}16$ plus a 0·6% paramagnetic-impurity correction. For $[\{Cu(ina)_2Br_2\}_n]$, the Heisenberg fit yielded a value of $J = -20{\cdot}2$ cm^{-1} with $g = 2{\cdot}15$ plus a 0·3% impurity correction. The e.p.r. spectra of both complexes consisted of one broad absorption centered at $\langle g \rangle = 2{\cdot}11$ for the chloride complex and at $\langle g \rangle = 2{\cdot}12$ for the bromide. Although the agreement between calculated and experimental g values is not as good for the ina complexes as for the Heisenberg results for na and pyzc,[1] the discrepancy is not so large as to invalidate the Heisenberg parameters calculated for $[\{Cu(ina)_2Cl_2\}_n]$ and $[\{Cu(ina)_2Br_2\}_n]$. A comparison of Heisenberg results for linear-chain $[\{CuL_2X_2\}_n]$ complexes is shown in the Table.

The similarities in magnetic and i.r. behaviour noted for these related species argue that the same *trans*-elongated linear structure must be present in all. Since

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Heisenberg parameters calculated for linear-chain $[\{CuL_2X_2\}_n]$ complexes

	J/cm^{-1}	g	Ref.
$[\{Cu(py)_2Cl_2\}_n]$	−9·15	2·05	16
$[\{Cu(py)_2Br_2\}_n]$	−18·9	2·11	16
$[\{Cu(pyzc)_2Cl_2\}_n]$	−10·7	2·12	1
$[\{Cu(pyzc)_2Br_2\}_n]$	−16·6	2·13	1
$[\{Cu(na)_2Cl_2\}_n]$	−10·1	2·09	*
$[\{Cu(na)_2Br_2\}_n]$	−20·6	2·14	*
$[\{Cu(ina)_2Cl_2\}_n]$	−5·2	2·16	*
$[\{Cu(ina)_2Br_2\}_n]$	−20·2	2·15	*

* This work.

the structures of $[\{Cu(py)_2X_2\}_n]$ ($X = Cl$ or Br) are known to be di-μ-halogeno-bridged one-dimensional polymers,[12,13] it is reasonable to postulate analogous structures for the na and ina complexes. Such a structure has been proposed for the pyzc complexes.[1] The postulated structure for the complexes $[\{Cu(na)_2X_2\}_n]$ and $[\{Cu(ina)_2X_2\}_n]$ is shown in Figure 3. Goodenough [23] demonstrated that antiferromagnetic exchange results when two d^9 cations interact *via* a single orbital of an anion even if the bridging cation–anion–cation angle is 90°. An exchange mechanism of this nature is consistent with the observed magnetic and spectral properties and with the postulated structures of the four complexes.

Examination of the exchange coupling constants in the Table reveals that the $|J|$ values for the bromide complexes are consistently higher than those of the corresponding chloride complexes. If the Cu–X–Cu angles in these complexes are similar to the 92° angle in $[\{Cu(py)_2Cl_2\}_n]$ [12] and the 93° angle in $[\{Cu(py)_2Br_2\}_n]$,[13] the stabilization of the singlet states in the bromide complexes can be understood in terms of the bridge-angle dependence observed for a series of hydrogen-bridged copper(II) complexes.[24] However, the problem is surely more complicated due to the different copper–halide bond lengths and the orbital energies of the halide bridges. It is clear that more structural data are required in order to interpret the variation in exchange coupling in these interesting linear-chain systems.

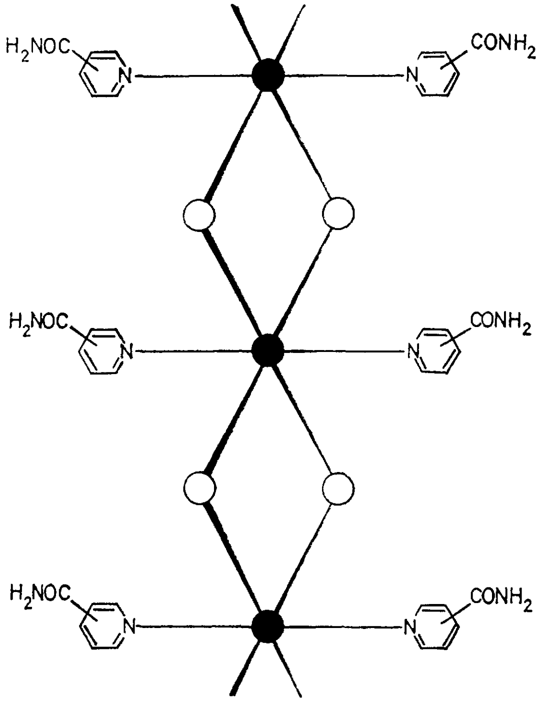

FIGURE 3 Proposed structure for the na and ina complexes of copper(II) halides (heavy lines do not imply bond lengths but indicate that the halide ion lies below the plane of the page)

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