Synthesis, Crystal Structure, Thermal Analysis and Magnetic Behavior of a Novel One-Dimensional Polymeric Pyridinium Chlorocuprate(II): $(Hpy)_2[Cu_3Cl_8(H_2O)_2]$

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A one-dimensional polymeric pyridinium chlorocuprate $(HPy)_2[Cu_3Cl_8(H_2O)_2]$, an intermediate between $(HPy)CuCl_3$ and $CuCl_2{\cdot}2H_2O$, has been synthesized and characterized by X-ray analysis [monoclinic, $P2_1/c$, a = 7.8950(10), b = 14.144(2), c = 9.921(10) Å, β = 99.20(2)°]. The structure contains $[Cu_3Cl_8(H_2O)_2]_n^{2n-}$ chains in which both square-pyramidal and octahedral Cu^{II} exist. The chains are composed of linked $[Cu_2Cl_6]^{2-}$ dimers and $CuCl_2(H_2O)_2$ monomeric units. On being heated in the solid state the compound undergoes dehydration followed by dehydrohalogenation to produce a pyridine complex of Cu^{II}: $[Cu_3Py_2Cl_6]$. Other compounds, $(HPy)_2[CuCl_4]$, $CuPyCl_2$ and $CuPy_2Cl_2$, also produce $[Cu_3Py_2Cl_6]$ as an intermediate on thermal analysis. Magnetic studies reveal ferromagnetic coupling within the chains with an intradimer exchange coupling of 12.1 cm^{-1} and a dimer-monomer exchange coupling of 1.34 cm^{-1}.

Introduction

The structural properties of chlorocuprates continue to be of interest, because of a wide variety of stereochemical features as well as unexpected oligomeric species.[1,2] However, most complexes for which structures have so far been reported contain copper atoms with a single coordination geometry, both in polymeric and in monomeric chlorocuprates.[3−7] Distorted octahedral, square-pyramidal, and trigonal-bipyramidal geometries of copper are known in polymeric chlorocuprates, whereas square-planar, square-pyramidal, and distorted tetrahedral anions have been reported with the monomeric $CuCl_{n+2}{}^{n-}$ complexes.[8−10] Among the hydrated chlorocuprates, the $CuCl_3(H_2O)^-$ species provides a novel intermediate between $CuCl_2(H_2O)_2$ and the $[CuCl_4]^{2-}$ anion.[11] On the other hand, the complexation of $CuCl_2{\cdot}2H_2O$ with pyridine and its derivatives has been studied extensively and the copper atoms in those complexes exhibit interesting structures.[12] With 2-picoline *N*-oxide it is found that $CuCl_2$ (when mixed in exactly 1:1 stoichiometric ratio) does not produce the expected 1:1 complex; instead a complex with empirical formula $Cu_3Cl_6(C_6H_7NO)_2{\cdot}2H_2O$ results, in which two types of copper atoms are present, one in an octahedral environment and the other in a square-pyramidal one. Here we report the synthesis, structure, and magnetic properties of the first example of a one-dimensional polymeric chain of hydrated chlorocuprates containing both hexa- and pentacoordinate copper atoms and possessing the empirical formula $(HPy)_2[Cu_3Cl_8(H_2O)_2]$, which can be regarded as a novel intermediate between $CuCl_2{\cdot}2H_2O$ and $(HPy)CuCl_3$, together with the solid-state synthesis of a new pyridine complex of Cu^{II}, $\{[Cu_3Py_2Cl_6]\}$, by thermal analysis.

Results and Discussion

The general method for the preparation of trichlorocuprates with cations of organic bases is to mix solutions containing the copper compound and a 1:1 molar ratios of the respective base acidified with HCl in aqueous or ethanolic medium. In the current case, however, the expected compound, $(HPy)CuCl_3$, is not produced by this method; instead a complex with empirical formula $(HPy)_2[Cu_3Cl_8(H_2O)_2]$ results. All attempts to prepare $(HPy)CuCl_3$ by changing the acidity of the solution and the ratio of pyridine:$CuCl_2{\cdot}2H_2O$ were unsuccessful.

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Description of the Structure of $(Hpy)_2[Cu_3Cl_8(H_2O)_2]$ (1): An ORTEP view of the complex **1** is shown in Figure 1. The complex consists of one-dimensional infinite chains that run parallel to the *c*-axis. These chains contain both six-coordinate (elongated octahedral) and five-coordinate (elongated square-pyramidal) copper ions bridged by the chlorine atoms. The six-coordinate copper ion (Cu1) is located on a center of inversion and bridged to two adjacent copper ions (Cu2) by pairs of chloride ions (Cl1, Cl2) and their inversion-related chloride ions. Two water molecules complete the distorted octahedral coordination around Cu1. Each five-coordinate copper ion (Cu2) is bridged to another five-coordinate copper ion by a pair of chloride ions (Cl4 and its inversion-related counterpart) with a center of symmetry between the pairs of Cu2 ions. Each Cu2 ion is bridged asymmetrically to Cu1 by two chloride ions. A non-bridging chloride ion (Cl3) occupies the fifth coordination site. The symmetry about the pentacoordinate copper ion (Cu2) is that of a square pyramid, with the three bridging chlorine atoms Cl2, Cl4, and Cl4 ($-x + 1$, $-y$, $-z$), and the non-bridging chlorine atom Cl3 forming the base of the pyramid and a bridging chlorine atom (Cl1) at the apex. The basal Cu−Cl distances lie in the 2.2681(8) to 2.3125(7) Å range and the apical Cu−Cl distance is 2.6770(8) Å (Table 1). The least-squares plane through Cl2, Cl3, Cl4, and Cl4($-x + 1$, $-y$, $-z$) is slightly puckered, with a maximum deviation of ±0.1447(8) Å for the two symmetry-related Cl4 atoms. The Cu2 atom is 0.2479(3) Å out of plane in the direction of the apex. The bond from the Cu2 ion to the chlorine atom Cl1 makes an angle of 88.9° with the basal plane. In the case of the hexacoordinate copper atom Cu1, the two chlorine atoms [Cl1 and Cl1($-x + 1$, $-y$, $-z - 1$)] and the two oxygen atoms [O and O($-x + 1$, $-y$, $-z - 1$)] define a perfect plane, since they lie on a center of symmetry. The apical chlorine atoms [Cl2 and Cl2 ($-x + 1$, $-y$, $-z - 1$)] on either side lie at a Cu−Cl distance of 2.8763(8) Å from the base plane. The compound, $(HPy)_2[Cu_3Cl_8(H_2O)_2]$, thus consists of $Cu_2Cl_6^{2-}$ dimers bridged by $CuCl_2{\cdot}2H_2O$ groups through two chlorine atoms, one from each unit, to form infinite chains. In other words, it can be regarded as an intermediate between $CuCl_2{\cdot}2H_2O$ and $CuCl_3^-$, since, of the three molecules of $CuCl_2{\cdot}2H_2O$, two form the dimeric trichlorocuprate anions $Cu_2Cl_6^{2-}$, while the third remains as a monomeric $CuCl_2{\cdot}2H_2O$ species. To the best of our knowledge, no chlorocuprate possessing this composition and structure has been reported to date. On the other hand, the structure of the 2-picoline *N*-oxide complex of Cu^{II}, $[Cu_3Cl_6(C_6H_7NO)_2]{\cdot}2H_2O$, is similar to that of the current complex.[12] It also consists of infinite chains containing both square-pyramidal five-coordinate and distorted octahedral six-coordinate copper ions. The only difference is that the two square-pyramidal copper ions are bridged by the oxygen atoms of two 2-picoline *N*-oxide ligands instead of the chloride ions in the present case.

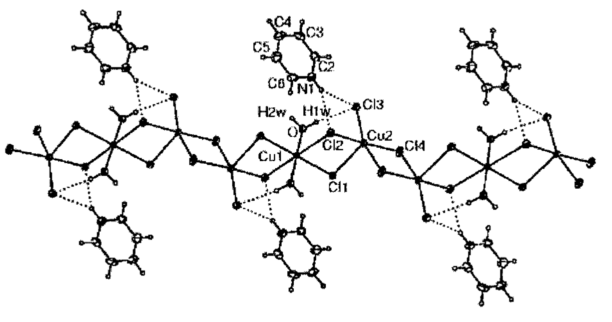

Figure 1. ORTEP drawing of the complex **1** with the atom numbering scheme; the bonds shown by dashed lines indicate hydrogen bonds; thermal ellipsoids shown at 50% probability

Table 1. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $(HPy)_2[Cu_3Cl_8(H_2O)_2]$

Cu(1)−O	1.978(2)
Cu(1)−Cl(2)	2.8763(8)
Cu(2)−Cl(2)	2.2681(8)
Cu(2)−Cl(4)	2.2952(8)
O−Cu(1)−Cl(1)	88.78(6)
O−Cu(1)−Cl(2)	93.90(7)
Cl(1)−Cu(1)−Cl(2)	84.00(3)
Cl(2)−Cu(2)−Cl(3)	91.43(2)
Cl(2)−Cu(2)−Cl(4)	172.80(3)
Cl(3)−Cu(2)−Cl(4)	90.77(2)
Cl(2)−Cu(2)−Cl(4)[a]	91.30(3)
Cl(3)−Cu(2)−Cl(4)[a]	160.76(3)
Cl(4)−Cu(2)−Cl(4)[a]	84.40(3)
Cl(2)−Cu(2)−Cl(1)	89.01(2)
Cl(3)−Cu(2)−Cl(1)	100.28(3)
Cl(4)−Cu(2)−Cl(1)	97.33(3)
Cl(1)−Cu(2)−Cl(4)[a]	98.80(3)
Cu(1)−Cl(2)−Cu(2)	87.97(3)
Cu(1)−Cl(1)−Cu(2)	92.78(3)
Cu(2)−Cl(4)−Cu(2)[a]	95.60(4)
Cu(1)−Cl(1)	2.2801(7)
Cu(2)−Cl(1)	2.6770(8)
Cu(2)−Cl(3)	2.2940(7)
Cu(2)−Cl(4)[a]	2.3125(7)

[a] Symmetry transformation used to generate equivalent atoms: $-x + 1$, $-y$, $-z$.

The crystal structure is stabilized by an extensive network of hydrogen bonds, with the Cl3 atom playing a key role, and also by stacking interactions (Figure 2, and Figure 3, Table 2). The Cl3 atom is the acceptor of two O−H···Cl hydrogen bonds, one from a water molecule of its own chain and the other from a water molecule of an adjacent chain related by a c glide plane. The pyridinium nitrogen atom is involved in a pair of bifurcated N−H···Cl hydrogen bonds with the Cl2 and Cl3 atoms of a polymeric chain acting as acceptors. The Cl3 atom thus accepts three hydrogen bonds: two from water molecules and one from a pyridinium ion. This is a good example of the principle of charge compensation that has been used to interpret the structures of copper(II) halides, in which the negatively charged halide ions compete for electrostatic interactions with the Cu^{II} ions and hydrogen bonding with the organoammonium ions.[13] It can also be observed that the pyridinium rings are stacked with the shortest distance between the centroids of two adjacent rings being 4.998(2) Å while the shortest perpendicular distance between the rings is 3.421 Å. This indicates a strong π-π interaction between the aromatic pyridinium moieties.

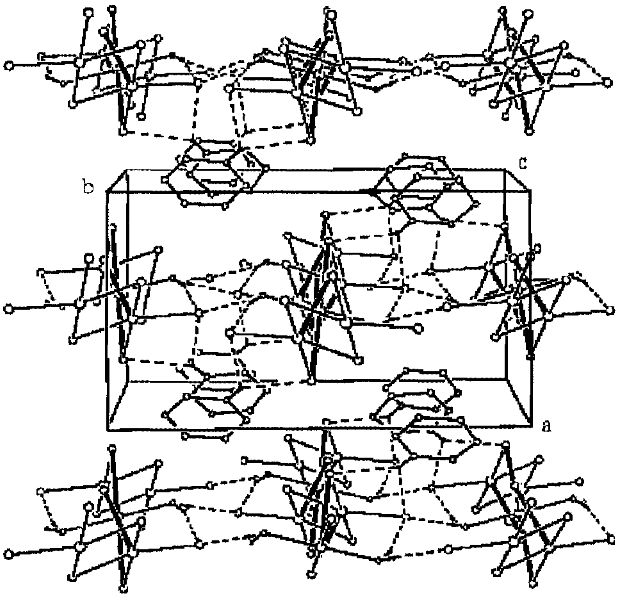

Figure 2. Crystal packing arrangement showing hydrogen bonding scheme and the stacking of pyridinium moieties; the dashed lines indicate hydrogen bonds

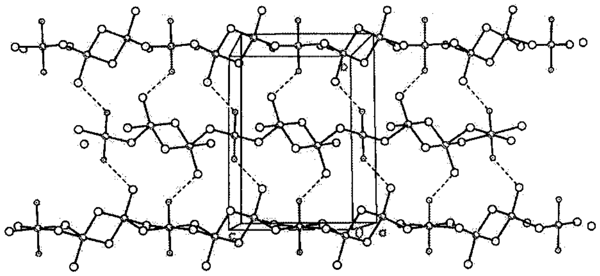

Figure 3. The interchain hydrogen bonding interaction; the dashed lines represent hydrogen bonds

Table 2. Hydrogen bonding distances (Å) and angles (°) for $(HPy)_2$-$[Cu_3Cl_8(H_2O)_2]$

D−H··· A	D−H	D···A	H···A	∠ D−H···A
O−H(1 W) ···Cl(3)	0.81(3)	3.132(2)	2.34(3)	165(3)
O−H(2 W) ···Cl(3)[a]	0.82(2)	3.184(2)	2.38(3)	169(2)
N(1)−H(1)···Cl(2)	0.860	3.189(3)	2.469	141.8
N(1)−H(1)···Cl(3)	0.860	3.345(3)	2.650	138.8

[a] Symmetry equivalents: x, $1/2 - y$, $-1/2 + z$.

IR and Electronic Spectroscopy

The electronic spectrum of compound **1** in Nujol mull shows three peaks with λ_{max} values at 24096, 18692, and 12004 cm^{-1}. The spectral pattern and peak positions are quite similar to those of brown dimeric trichlorocuprate ($Cu_2Cl_6^{2-}$), with a square-pyramidal structure and an empirical formula of $(HBz)_2Cu_2Cl_6$ {Bz = benzimidazolium[6]}. The spectrum of **1** is therefore totally dominated by the square-pyramidal copper(II), which obscures the weak Laporte-forbidden transitions originating from the centrosymmetric octahedral copper(II) portion of compound **1**.

The spectrum of $[Cu_3Py_2Cl_6]$ (**1a**) shows two peaks with λ_{max} values at 23981 and 11723 cm^{-1}. Although it is very difficult to infer the exact structure of this type of complex, the presence of flattened tetrahedral (D_{2d}) copper(II) may be predicted from the lower energy of the d−d transition.[1] In addition, the band in the 24000 cm^{-1} region is indicative of the presence of doubly bridged $Cu-(Cl)_2-Cu$ or $Cu-(Cl)_3-Cu$ linkage.

IR spectra of **1** show a broad band due to the OH stretching modes of water molecules at 3301cm^{-1}. The appearance of the peak at lower wavelength corroborates the presence of extensive hydrogen bonding as found by single-crystal X-ray diffraction.

Thermal Analyses

The TG curves of the compounds $(HPy)_2[Cu_3Cl_8(H_2O)]_2$, $(HPy)_2[CuCl_4]$, $CuPyCl_2$, and $CuPy_2Cl_2$ are given in Figure 4. The thermal behavior of compound **1** shows that the compound loses its water molecules at ca. 105 °C (obsd. loss 5.6%; calcd. 5.4%) to produce the dehydrated compound $(HPy)_2Cu_3Cl_8$ (Table 3), which on being kept in a humid atmosphere (relative humidity $> 50\%$) for several hours at ambient temperature absorbs exactly two molecules of water per three copper atoms to revert to **1**. The process is thus reversible. The X-ray powder diffraction pattern of **1** differs considerably from that of its anhydrous analogue $(HPy)_2Cu_3Cl_8$, but is identical to that of the rehydrated species. As the coordinated water molecules from the hexacoordinate copper (Cu1) are removed on dehydration, there should be a drastic change in the coordination geometry around this copper atom, and it is probably this that is reflected in the difference between the diffraction patterns. However, the structural skeleton of **1** must be retained on dehydration because on being kept in moist atmosphere, compound **1** is obtained again, as is confirmed by the identical diffraction patterns of the re-hydrated species and **1**. It is a reasonable assumption that the structure collapses to one analogous to the $A_nCu_{n+1}Cl_{3n+2}$ structures, in which a repeat sequence of n tribridged units and one bibridged unit occurs in the chain structure.[14] On further heating, $(HPy)_2Cu_3Cl_8$ undergoes dehydrohalogenation (obsd. loss 11.40%; calcd. 10.9%) at ca. 190 °C to produce $[Cu_3Py_2Cl_6]$. It is to be noted here that the pyridine ligand, after losing its proton as HCl, enters into the coordination sphere of the copper(II) in the solid state to yield the pyridine complex **1a**. This compound is thermally stable up to ca. 240 °C, after which it finally decomposes to $CuCl_2$.

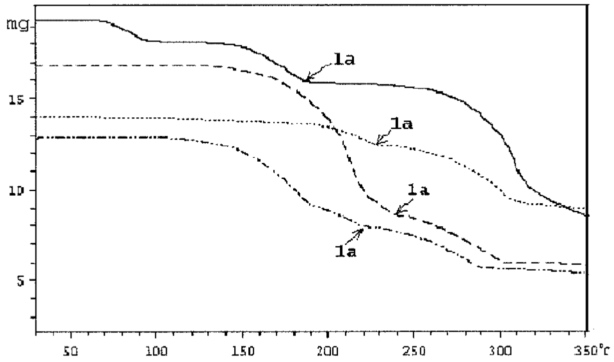

Figure 4. The TG curves: – –, $(HPy)_2[Cu_3Cl_8(H_2O)_2]$; -----, $(HPy)_2[CuCl_4]$; ●●●●●●●, $[CuPyCl_2]$ and - ●● - ●● –, $[CuPy_2Cl_2]$; the labels **1a** denote the temperature at which $[Cu_3Py_2Cl_6]$ is formed

Table 3. Results of thermal analysis of compounds **2**, **3** and **4**

Thermal reactions	Temp. range (°C)	Weight loss (%) Obsd.	Calcd.
$(PyH)_2[CuCl_4]$ (2) → $CuPyCl_2$	150–220	42.20	41.59
$3CuPyCl_2$ → $[Cu_3Py_2Cl_6]$	220–250	6.60	7.20
$[Cu_3Py_2Cl_6]$ → $3CuCl_2$	250–305	14.50	14.41
$3CuPyCl_2$ (3) → $[Cu_3Py_2Cl_6]$	190–235	11.40	12.33
$[Cu_3Py_2Cl_6]$ → $3CuCl_2$	245–310	25.50	24.67
$CuPy_2Cl_2$ (4) → $CuPyCl_2$	125–190	26.80	27.00
$3CuPyCl_2$ → $[Cu_3Py_2Cl_6]$	190–220	9.30	9.00
$[Cu_3Py_2Cl_6]$ → $3CuCl_2$	225–293	18.25	18.00

The interesting feature of the thermal analysis is the isolation of $[Cu_3Py_2Cl_6]$ (**1a**), which can be synthesized in the solid state from **1** as discussed in the preceding paragraph. Any attempt to synthesize compound **1a** in solution, either by the addition of pyridine and $CuCl_2{\cdot}2H_2O$ in 2:3 ratio or by crystallization of the title compound from common solvents (methanol, ethanol, water etc.) always results in $CuPyCl_2$ (see Exp. Sect.). Recrystallization of **1a** also results in $CuPyCl_2$. The X-ray powder diffraction results for compounds **1a**, **3**, and anhydrous $CuCl_2$ show that $[Cu_3Py_2Cl_6]$ is not a mixture of $CuPyCl_2$ and $CuCl_2$. It is relevant to mention here that complexes of composition $[M_3Py_2Cl_6]$ have been prepared by pyrolytic techniques with Cr^{II}, Mn^{II}, Co^{II}, Ni^{II}, and Cd^{II}.[15] With copper(II), though, it was thought that the existence of such complexes is not possible, as it does not form regular octahedral complexes because of Jahn–Teller effects.[16] Also, in a recent paper, no isolable intermediate was detected in the thermal analysis of $(Hpy)_2[CuCl_4]$.[17] However, the thermal analysis results for $(HPy)_2[Cu_3Cl_8(H_2O)_2]$, $(HPy)_2[CuCl_4]$, $CuPyCl_2$, and $CuPy_2Cl_2$ presented in this paper show that all of them finally decompose to $CuCl_2$ via the intermediate species $[Cu_3Py_2Cl_6]$. Only compound **1** permits isolation of **1a** in the pure state upon being heated, however, as the TG curve for **1** shows a plateau in the temperature range in which **1a** is stable. Earlier failure in its isolation was therefore a result of the decomposition temperature of copper(II)-pyridine complexes and had nothing to do with the Jahn–Teller effect.

Magnetic Behavior

The plot of $\chi_M T$ vs. T in Figure 5 reveals the presence of ferromagnetic interactions within the system. The value of $\chi_M T$ increases monotonically as T is lowered, with no maximum observed down to 1.9 K. Thus, no significant antiferromagnetic coupling appears to exist in this material. The M vs. H curve at 2.0 K (Figure 6) rises smoothly to a saturation value of $M_{satd.} \approx 3.05\ \mu_B$, giving no evidence for significant spin canting nor for a ferrimagnetic ground state of the chain system.

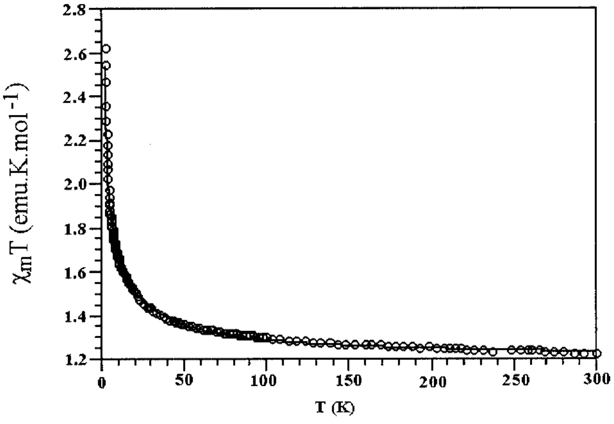

Figure 5. Plot of $\chi_M T$ vs. T for $(HPy)_2[Cu_3Cl_8(H_2O)_2]$; solid line is the calculated curve

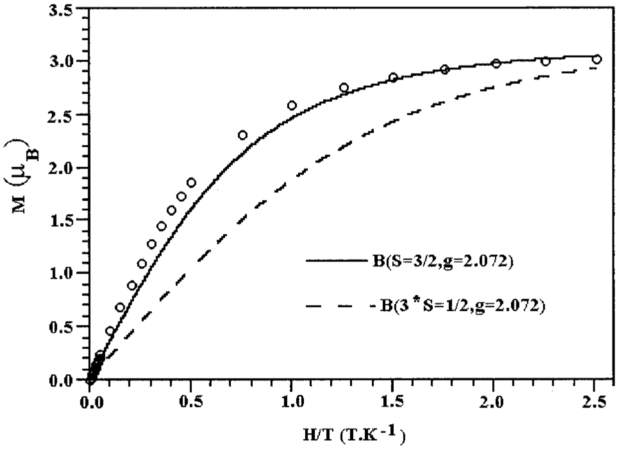

Figure 6. Plot of M vs. H/T at 1.8 K for $(HPy)_2[Cu_3Cl_8(H_2O)_2]$; solid line and dashed line are the calculated Brillouin functions

The data in Figure 5 can be fitted very satisfactorily by use of a model for a chain of alternating dimer and monomer units. The procedure consisted of treatment of the infinite chain as a ring of finite length by use of a closed-chain computational procedure. The infinite chain behavior can be obtained by extrapolation from the exact result for increasing ring length.

$$\hat{H} = -2\sum_{i=0}^{N-1}\left[J_1\hat{S}_{3i}\hat{S}_{3i+1} + J_2\left(\hat{S}_{3i+1}\hat{S}_{3i+2} + \hat{S}_{3i+2}\hat{S}_{3i+3}\right)\right]$$

The exchange Hamiltonian may be written as where 3 N corresponds to the number of interacting spins. J_1 is the intradimer exchange interaction, and J_2 is the interaction between the dimer and the monomer. The calculations are limited up to 18 spins ($N = 6$). Evaluation of the susceptibility curves was performed by use of the MAGPACK programs package.[18] The differences between the curves with $N = 4$ and 6 are less than 0.2% over the full range of temperatures, so the $N = 6$ ring is taken as the exact solution for the infinite change in the experimental temperature range. Under these considerations the best fit obtained by a least-squares analysis of the $\chi_m T$ data is $J_1 = 17.35$ K = 12.1 cm^{-1} (intradimer exchange constant), $J_2 = 1.93$ K = 1.34 cm^{-1} (dimer−monomer exchange constant), $g = 2.072$, and $R = 5.76 \times 10^{-5}$.

The magnetization data (Figure 6) can be compared with the Brillouin function expected for three independent Cu^{II} ions (dashed line) and with a $S = 3/2$ system (solid line). As can be seen, the agreement is much better, as would be expected, for a $S = 3/2$ system, although the experimentally measured values are slightly above the theoretical ones at low fields. This may be due to the presence of the extended interactions within chains that cannot be taken into account with a simple Brillouin function.

Magneto-Structural Correlations

The magnetic studies indicate the presence of ferromagnetic coupling both within the dimeric species and between the dimer and monomer units. Correlation of the exchange coupling with structural parameters in $Cu_2Cl_6^{2-}$ dimers has received considerable attention in the past.[19] The coupling is antiferromagnetic, with $J/k \approx 50$ K for the planar conformation (based on the interaction Hamiltonian $H = -J\,\mathbf{S}_1\cdot\mathbf{S}_2$), with the coupling becoming ferromagnetic as distortion from planarity occurs. In particular, for the type of bifold distortion observed in this structure, the crossover is estimated to occur at a bifold angle near 20°. Thus, with a bifold angle of 19.7°, the presence of ferromagnetic coupling within the dimer is consistent with the previous studies. For the dimer/monomer coupling, this pathway is analogous to those found in asymmetric bibridged dimers and chains.[20] This coupling can be either ferro- or antiferromagnetic, depending on details of the pathway (although no simple magneto-structural correlations exist). When the coupling is ferromagnetic, the magnitude of the coupling is invariably small, in agreement with these results.

Finally, it should be noted that hydrogen-bonded Cu−Cl···H$_2$O−Cu linkages occur between chains (Figure 3). In the absence of any decrease in $\chi_M T$ as $T \rightarrow 0$ K, it is clear that this interaction must also be ferromagnetic. The J' value may thus also include some small contribution from this pathway.

Discussion

The magnetic properties of this system can be compared with those of several other previously examined trimer-type chain systems. The $(Cu_2X_6)Cu(TMSO)_4$ system (TMSO = tetramethylenesulfone) contains chains of $Cu_2X_6^{2-}$ anions bridged by $Cu(TMSO)_4^{2+}$ cations.[21] For these compounds, the Cu^{II} ions in the cations have distorted tetrahedral geometries, which results in quite strong ferromagnetic coupling within the $Cu_2X_6^{2-}$ dimers. The cations and anions are linked by bent Cu−X···Cu interactions, giving ferromagnetic dimer/monomer coupling for the chloride salt, but weak antiferromagnetic coupling is observed at low temperatures in the bromide salt (although this antiferromagnetic coupling may, in reality, be propagated through a short interchain Br···S contact). Thus, the chloride salt behaves as a ferromagnetic chain, while the bromide exhibits ferrimagnetic behavior.

In $[Cu_3Cl_6(dioxane)_2]$, a complex bi-bridged chain with a ferro/ferro/antiferro repeat pattern exists.[22] With J(ferro) >> J(antiferro), the system effectively behaves as an antiferromagnetic $S = 3/2$ chain at low temperature. This can be contrasted with the behavior of the ferrimagnetic trimer chain in (N-methyl-2-picolinium)$_2$Cu$_3$Br$_8$.[23] Here, strong antiferromagnetic interactions exist within the planar bibridged $Cu_3Br_8^{2-}$ trimer units, stabilizing a $S = 1/2$ ground state. These are then coupled together in a ferromagnetic fashion, to give a system that behaves as a $S = 1/2$ ferromagnetic chain at low temperature. In addition, there are numerous other known $A_2Cu_3X_8$ salts containing planar bibridged trimers, in which the antiferromagnetically coupled trimers stack in complex fashions, for which the magnetic properties have not been thoroughly analyzed.[24]

Experimental Section

Materials and Measurements: High purity (98%) pyridine and copper(II) chloride dihydrate were purchased from E. Merck, Germany and were used as received. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin−Elmer 240C elemental analyzer and the copper contents in all the complexes were estimated spectrophotometrically.[25] IR spectra in KBr (4500−500 cm^{-1}) were recorded with a Perkin−Elmer RXI FT-IR spectrophotometer. Electronic spectra (1200−350 nm) were recorded with a Hitachi U-3501 spectrophotometer in Nujol mull. The thermal analyses (TG-DTA) were carried out with a Mettler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 30 cm^3 min^{-1}). The sample was heated in an alumina crucible at a rate of 5 °C min^{-1}. The X-ray powder diffraction experiments were carried out on a Philips PW 3710 diffractometer equipped with a copper tube anode. Variable-temperature susceptibility measurements were carried out for $(HPy)_2Cu_3Cl_8\cdot 2H_2O$ in the 2−300 K temperature range at a magnetic field of 0.1 T on ground polycrystalline samples with a SQUID magnetometer (Quantum Design MPMS-XL-5). The susceptibility data were corrected for the diamagnetic contributions deduced by use of Pascal's constant tables. Isothermal magnetization and hysteresis measurements were made for $(HPy)_2Cu_3Cl_8\cdot 2H_2O$ at different temperatures, after zero field cooling between 0 and 5 T in the SQUID magnetometer.

Preparations

$(HPy)_2[Cu_3Cl_8(H_2O)_2]$ (Brown) (1): $CuCl_2\cdot 2H_2O$ (5 mmol) was dissolved in a minimum volume of water. Pyridine (5 mmol) was mixed into this solution, along with concentrated HCl (4 mL). The resulting solution was concentrated in a water bath to ca. 5 mL and kept in a desiccator. After a few days reddish-brown shiny single crystals suitable for X-ray diffraction were obtained. $C_{10}H_{16}Cl_8Cu_3N_2O_2$ (670.5): calcd. C 17.9, H 2.4, N 4.2, Cu 28.4; found C 18.0, H 2.3, N 4.3, Cu 27.8. λ_{max} = 24096, 18692, 12005 cm^{-1}

[$Cu_3Py_2Cl_6$] (Pale Green) (1a): This compound was prepared by heating of compound **1** for 30 min at ca. 190 °C. $C_{10}H_{10}Cl_6Cu_3N_2$ (561.5) : calcd. C 21.4, H 1.8, N 5.0, Cu 33.9; found C 21.2, H 1.9, N 5.1, Cu 33.6. λ_{max} = 23981 and 11723 cm^{-1}.

$(HPy)_2[CuCl_4]$ (Yellow) (2): This compound was prepared by the same procedure as used in the case of compound **1** except that $CuCl_2{\cdot}2H_2O$ and pyridine were used here in 1:2 molar ratio. $C_{10}H_{12}Cl_4CuN_2$ (365.5): calcd. C 32.8, H 3.3, N 7.7, Cu 17.4; found C 32.5, H 3.2, N 7.4, Cu 17.0. λ_{max} = 24390 and 9200 cm^{-1}.

$CuPyCl_2$ (Pale Yellow) (3) and $CuPy_2Cl_2$ (Blue) (4): The compounds were synthesized by mixing of ethanol solutions of $CuCl_2{\cdot}2H_2O$ and pyridine in the required molar ratios. The compounds can also be synthesized by shaking the compounds **1** and **2** respectively in ethanol. **3:** $C_5H_5Cl_2CuN$ (213.5): calcd. C 28.1, H 2.4, N 6.6, Cu 29.7; found C 28.0, H 2.1, N 6.4, Cu 29.5. UV: λ_{max} = 23585, 20747, 14970, 11723, 10953 cm^{-1}. **4:** $C_{10}H_{10}Cl_2CuN_2$ (292.7): calcd. C 41.0, H 3.4, N 9.6, Cu 21.7; found C 41.0, H 3.6, N 9.4, Cu 21.5. λ_{max} values are as reported in the literature[26] for **4**.

X-ray Crystallography: A suitable single crystal of the complex **1** was mounted on a Bruker AXS CCD area detector system for data collection. The crystal data of the complex were collected at 293(2) K. Intensity data were collected in the ω scan mode by use of graphite-monochromated Mo-K_α radiation (0.71073 Å). The empirical absorption corrections were based on Ψ scans. The structure was solved by SIR-97[27] methods and refinement was made with the SHELXL-97 suite of programs. Anisotropic full-matrix refinements based on F^2 were carried out for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and refined in the "riding" model with isotropic thermal parameters 1.2 times U_{eq} of the atom to which they were attached. Complex neutral atom scattering factors were used throughout the refinement. All calculations were carried out with the aid of the SHELX 97,[28] PLATON 99[29] and ORTEP[30] programs. Selected crystallographic data for complex **1** are displayed in Table 4, while selected bond lengths and bond angles of the complex are presented in Table 1. The H-bonding and non-bonding contacts of **1** are listed in Table 2. CCDC-170243 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data and structure refinement details of $(HPy)_2[Cu_3Cl_8(H_2O)_2]$

Empirical formula	$C_5H_8Cl_4Cu_{1.5}ON$
Molecular mass	335.23
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 7.8950(10) Å b = 14.144(2) Å c = 9.9210(10) Å β = 99.20(2)°
V	1093.6(2) Å^3
Z, calculated density	4, 2.036 Mg/m^3
Absorption coefficient	3.876 mm^{-1}
F(000)	658
Crystal size	0.21 × 0.17 × 0.11 mm
Crystal color	brown
θ range for data collection	2.53 to 28.09°
Limiting indices	$-10 \leq h \leq 10$ $-18 \leq k \leq 18$ $-12 \leq l \leq 12$
Reflections collected/unique	11396/2460
R(int)	0.0406
Completeness to θ = 28.09°	92.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2460/2/121
Goodness-of-fit on F^2	1.105
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0277, wR_2 = 0.0708
R indices (all data)	R_1 = 0.0329, wR_2 = 0.0740
Largest diff. peak and hole	0.467 and −0.610 eÅ $^{-3}$

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