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Synthesis, crystal structure and magnetic properties of 1-(2,5-dimethylphenyl)piperazine-1,4-dium tetrachloridocuprate(II)

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Abstract. The synthesis and physico-chemical characterization of a novel organic-inorganic hybrid material, 1-(2,5-dimethylphenyl)piperazine-1,4-dium tetrachloridocuprate(II), have been reported. This compound crystallizes in the monoclinic system with the space group of $P2_1/n$ and cell parameters $a = 9.833(3)$, $b = 16.337(2)$, $c = 10.452(3)$ Å, $\beta = 102.13(4)°$, $Z = 4$ and $V = 1641.5(7)$ Å^3. In the title salt, $(C_{12}H_{20}N_2)[CuCl_4]$, the geometry of the $CuCl_4^{2-}$ ion is intermediate between tetrahedral and square planar. In the atomic arrangement tetrachlorocuprate anions and the piperazine-1,4-dium cations are held together *via* N-H...Cl and C-H...Cl to give a 1-D hybrid chain running along the *a*-axis. The six-membered piperazinedium ring adopts a chair conformation. The vibrational absorption bands were identified by infrared spectroscopy. Magnetic measurements reveal that moderate antiferromagnetic (AF) Cu–Cu interactions dominate in the title compound.

Keywords. Cu(II) complex; X-ray diffraction; FT-IR; magnetic properties.

1. Introduction

Non-covalent interactions, such as hydrogen bonding, play a very prominent role in the organization of structural units in biochemistry and material science.[1–3] These weak interactions exercise important effects on the architecture and properties of many materials in various fields such as biology[4,5] and crystal engineering.[6,7] The control of these interactions will be important for the design of materials with specific types of properties such as conductivity or magnetic behavior.[8] Several works were focused on copper(II) halides to study the influence of the organic cations on the packing interactions that govern the structural organization and consequently on the properties of this kind of complex.[9,10] The Cu(II) complexes have different molecular geometries, such as tetrahedral, square planar, square pyramidal and octahedral.[11]

Recently, some studies have examined how the metal halide compounds, of the general formula A_2MX_4 where A is an organic cation, M is a divalent metal, and X is a halogen, can be tied together *via* organic cations into chains, layers, etc.[12] These compounds exhibit interesting magnetic properties which are related to the inter-halide distances between the MX_4^{2-} anions, which in turn are strongly related to the properties of the organic cation.[13–15]

It is well-known that organic-inorganic materials with nitrogen ligands as template agents have led to the preparation of some materials with interesting physical properties[16–20] and biological activities.[21–23] Furthermore, complexes containing transition metals may be formed by bridging ligands that can mediate magnetic interactions between paramagnetic metal ions.[24] Another aspect that makes especially copper(II) complexes quite interesting is that many complexes have been found to have the potential for treatment of cancers and other diseases,[25] and these complexes have drawn great attention for their high nucleolytic efficiency.[26–35] The transition metal complexes, especially copper(II) complexes, are known to be effective against rheumatoid arthritis and they also show anti-ulcer activity.[36,37] These Cu(II) complexes have different molecular geometries, such as tetrahedral, square planar, square pyramidal and octahedral.[38]

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In connection with studies on the structural aspect of halo-metal anion salts containing nirtogen ligands,[39–42] we herein report the crystal structure of $(C_{12}H_{20}N_2)[CuCl_4]$ and its IR spectroscopic, and magnetic characterizations.

2. Experimental

2.1 *Preparation of title compound*

To an aqueous solution (10 mL) of HCl (0.2 M) was added 1-(2,5-dimethylphenyl)piperazine (0.19 g, 1 mmol). To this solution, a blue aqueous solution (10 mL) of $CuCl_2.6H_2O$ (0.170 g, 1 mmol) was added slowly with stirring. The resulting solution was evaporated slowly at room temperature until the formation of green crystals of the title compound. (yield = 73%).

Anal. Calc. (%): C, 36.21; H, 5.03; N, 7.04%. Found (%): C, 36.54; H, 5.31; N, 7.29.

2.2 *X-ray single crystal structural analysis*

A single crystal was used for X-ray measurements. The intensity data collection was performed with a MACH3 Enraf-Nonius diffractometer operating at 292 K with the wavelength $K\alpha$ (Ag) = 0.5608 Å. Structure was solved by direct methods using the SIR92[43] program and refined by full matrix least-squares techniques based on F^2 with SHELXL software.[44] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were constrained to calculated positions and refined using riding models. Relevant crystallographic structure data and refinement details are presented in table 1.

Table 1. Crystal data, intensity collection parameters and refinement results for $(C_{12}H_{20}N_2)[CuCl_4]$.

Crystal data	
Empirical formula	$C_{12}H_{20}Cl_4CuN_2$
Formula weight (g.mol^{-1})	397.64
Crystal system/space group	monoclinic/$P2_1/n$
a (Å)	9.833(3)
b (Å)	16.337(2)
c (Å)	10.452(3)
β (deg.)	102.13(4)
Volume (Å^3)	1641.5(7)
Z	4
Density (calc.) (g cm^{-3})	1.609
F(000)	812
$\theta-$Range for data collection (deg.)	9-11
Morphology	prism
Color	blue
Crystal size (mm)	$0.25 \times 0.15 \times 0.10$
II- Intensity measurements	
Temperature	293
Diffractometer	EnrafNonius MACH 3[43]
Monochromator	graphite plate
Wavelength	AgKα (0.56087 Å)
Theta range (°)	2.04-27.96
Index ranges:$-16 \le h \le 16$, $-2 \le k \le 27$, $-3 \le l \le 17$	
Reflections collected	11520
Independent reflections	8047
III- Structure determination	
No absorption corrections	
Program used	SHELXL-97[44]
Determination: direct methods	
Observed reflections[$I > 2\sigma(I)$]	3892
Refined parameters	172
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0627$; $wR_2 = 0.1420$
Largest shift/error	0.000
Goodness-of-fit on F^2	1.008

2.3 *Infrared spectroscopy*

The IR spectrum was recorded in the range 4000–400 cm^{-1} with a Perkin–Elmer FTIR spectrophotometer 1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.
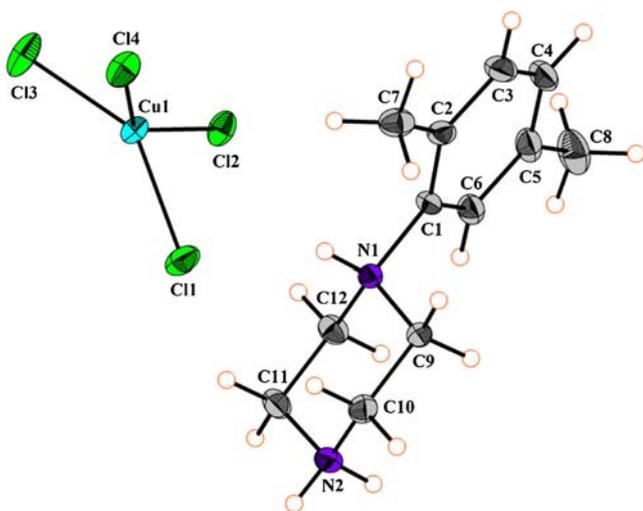
2.4 *Magnetic properties*

The magnetic properties of powder samples were investigated on a Quantum Design MPMS-7T superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–300 K with an external field of 1000 Oe.

3. Results and Discussion

3.1 *X-ray diffraction study*

The structure of $(C_{12}H_{20}N_2)[CuCl_4]$ consists of discrete $CuCl_4^{2-}$ anions and 1-(2,5-dimethylphenyl)piperazine-1,4-dium cations (figure 1). The copper(II) has a coordination geometry intermediate between tetrahedral and square planar. The trans bond angles are 146.56(6)° for Cl1-Cu1-Cl3 and 140.50(6)° for Cl2-Cu1-Cl4 (table 2). The Cu-Cl bond lengths range from 2.230(1) to 2.254(1) Å (table 2). The variation of these geometric parameters is attributed to the environment differences around the chlorine atoms.

In the atomic arrangement, the anionic species link the piperazine-1,4-dium cations *via* N-H...Cl and C-H...Cl to give a 1-D hybrid chain running along the

Table 2. Selected geometric parameters (Å, °) in $(C_{12}H_{20}N_2)[CuCl_4]$.

Cu1-Cl1	2.2459(12)	C1-C6	1.378(5)
Cu1-Cl2	2.2539(12)	C2-C3	1.403(5)
Cu1-Cl3	2.2488(13)	C2-C7	1.499(5)
Cu1-Cl4	2.2303(13)	C3-C4	1.380(6)
N1-C1	1.503(4)	C4-C5	1.385(6)
N1-C9	1.513(4)	C5-C6	1.387(5)
N1-C12	1.503(4)	C5-C8	1.501(6)
N2-C10	1.485(5)	C9-C10	1.507(4)
N2-C11	1.485(5)	C11-C12	1.517(4)
C1-C2	1.395(5)		
Cl1-Cu1-Cl2	94.50(5)	C1-C2-C7	124.7(3)
Cl1-Cu1-Cl3	146.65(6)	C1-C2-C3	115.3(3)
Cl1-Cu1-Cl4	95.67(6)	C3-C2-C7	120.0(3)
Cl2-Cu1-Cl3	95.97(6)	C2-C3-C4	121.8(4)
Cl2-Cu1-Cl4	140.50(6)	C3-C4-C5	121.8(4)
Cl3-Cu1-Cl4	96.12(6)	C4-C5-C8	122.0(4)
N1-C1-C2	117.8(3)	C4-C5-C6	117.2(3)
N1-C1-C6	119.2(3)	C6-C5-C8	120.8(4)
N1-C12-C11	111.1(3)	C1-C6-C5	120.8(3)
N1-C9-C10	111.4(3)	N2-C10-C9	110.6(3)
C9-N1-C12	110.4(3)	N2-C11-C12	110.1(3)
C1-N1-C9	109.3(2)	C10-N2-C11	111.0(3)
C1-N1-C12	113.9(2)	C2-C1-C6	123.0(3)

a-axis direction (figure 2). The 2,5-dimethylphenyl groups are located between these chains and are not involved in H-bonding interactions (figure 3, table 3). The projection of the structure along the *c*-axis direction (figure 4) shows that the $CuCl_4^{2-}$ anions are grouped in pairs. These lie at (1/4, 1/4, 0) and (3/4, 3/4, 0). Within the network, the 1-(2,5-dimethylphenyl)piperazine-1,4-dium cations are arranged into antiparallel dimers (figure 3). No significant $\pi - \pi$ stacking interactions between the phenylene rings, nor C-H...π interactions are observed.

Regarding the hydrogen bonds network, table 3 shows that all the chlorine atoms of the $CuCl_4^{2-}$ anions are involved in H-bonding interactions. The Cl1 is a triple acceptor, the Cl2 and Cl4 are double acceptors, while the Cl1 is involved in only one hydrogen bond. Among these hydrogen bonds one is bifurcated N-H2B...(Cl3, Cl4).

All the bond lengths and angles of the organic entity (table 2) agree with those found in another salt containing the same cation, 1-(2,5-dimethylphenyl)piperazine-1,4-dium tetrachlorozincate monohydrate.[45] The conformation of the piperazinedium six-membered ring can be described in terms of Cremer and Pople puckering coordinates,[46] *i.e.*, evaluating the parameters Q (total puckering amplitude), q2, q3, θ and φ. The calculated values for C1–C2–C3–N1–C4–C5 ring are as follows: Q = 0.571 Å, q2 = 0.022 Å, q3 = 0.571 Å, $\theta = 2.25°$

Figure 1. A view of the asymmetric unit in the crystal structure of $(C_{12}H_{20}N_2)[CuCl_4]$ showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.
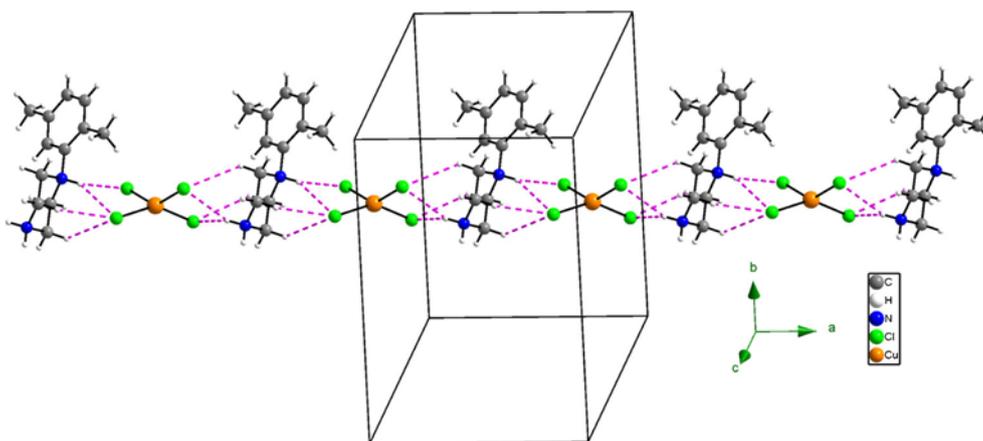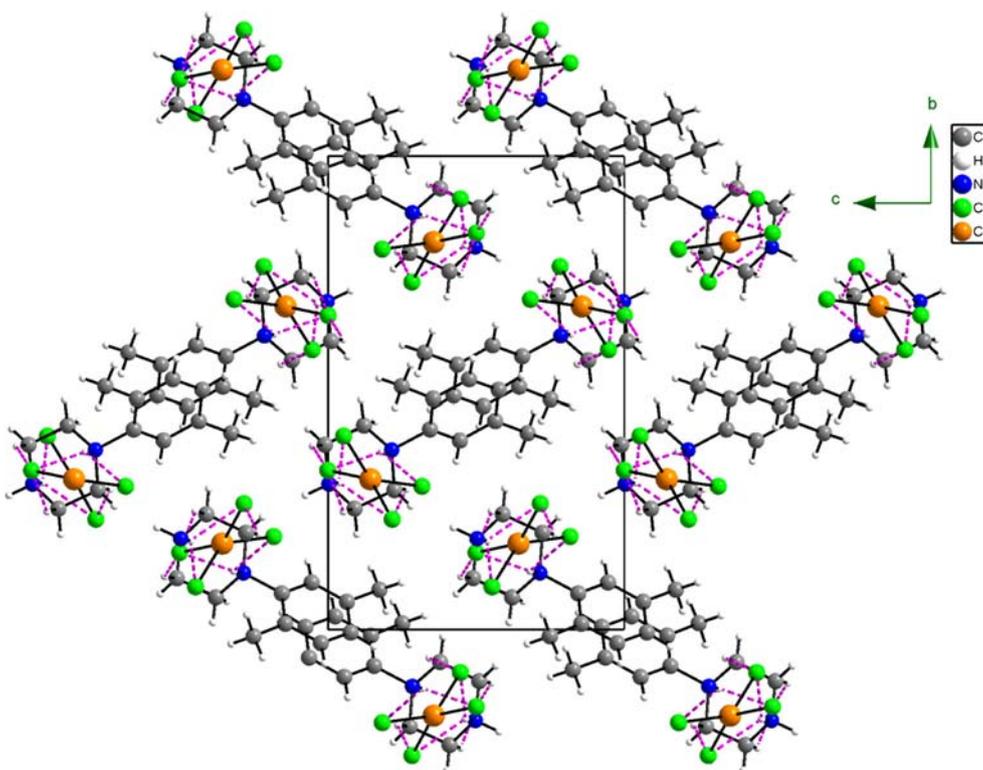
Figure 2. A view of 1-D hybrid chain running in $(C_{12}H_{20}N_2)[CuCl_4]$.
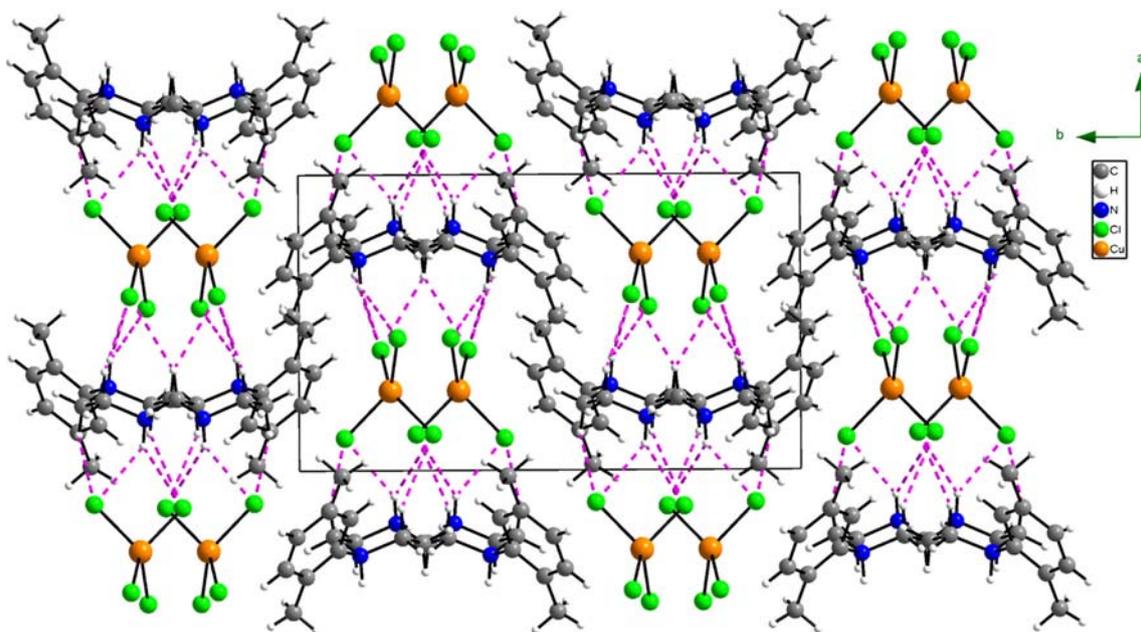

Figure 3. Projection along the *a*-axis of the crystal packing of the title compound. The dotted lines indicate hydrogen bonds.

Table 3. Hydrogen-bond geometry (Å, °) in $(C_{12}H_{20}N_2)[CuCl_4]$.

| D-H···A	D-H	H···A	D···A	D-H···A
N1-H1···Cl1	0.9100	2.5900	3.427(3)	153.00
N1-H1···Cl2	0.9100	2.7100	3.274(3)	121.00
N2-H2B···Cl3[i]	0.9000	2.7900	3.534(3)	141.00
N2-H2B···Cl4[i]	0.9000	2.4900	3.236(3)	141.00
C9-H9A···Cl4[i]	0.9700	2.8100	3.519(3)	131.00
C10-H10B···Cl1	0.9700	2.7800	3.590(4)	142.00
C11-H11A···Cl1	0.9700	2.7800	3.590(4)	142.00
C12-H12A···Cl3[i]	0.9700	2.8200	3.590(4)	138.00

Symmetry code: (i) $x-1, y, z$.

Figure 4. Projection along the *c*-axis of the crystal packing of the title compound. The dotted lines indicate hydrogen bonds.

and $\varphi = -157.82°$ corresponding to the structure of the most stable chair conformation.

3.2 *IR spectroscopy*

FTIR spectroscopy was used to verify the functional groups present in the crystal and to investigate their vibrational behavior in the solid state. The IR spectrum of the title crystalline complex is shown in figure 5. The characteristic vibrational modes of this compound can be compared to those of similar materials.[47–49] The very large bands in the high-frequency region, spreading between 3600 and 2600 cm^{-1}, correspond to the stretching vibrations of the N-H and C-H groups
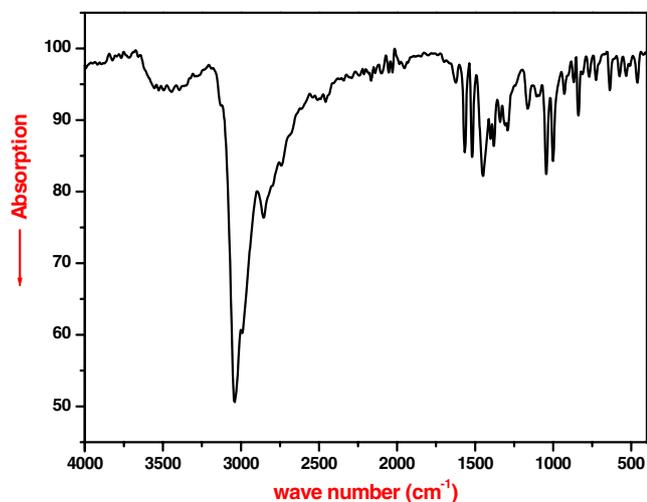

Figure 5. Infrared spectrum of $(C_{12}H_{20}N_2)[CuCl_4]$.

interconnected by a system of hydrogen bonds in the crystal.[50] The band at 1623 cm^{-1} is assigned to the N-H bending mode. The bands observed in the 1570 and 1050 cm^{-1} region can be assigned to the valence vibrations of the C=C, C=N, C-C, C-N bonds and to the wagging and rocking modes of the CH_2 groups.[51] The observed bands in the range 1000–600 cm^{-1} can be assigned to the CH_3 and NH_3^+ groups and to the skeleton of phenylene rings symmetric, asymmetric, stretching and deformation modes[52,53] and to the CH_2 rocking modes.[54]

3.3 *Magnetic properties*

The title compound shows linear Curie–Weiss behavior in the χ^{-1} vs. T plot in the temperature range of 35–290 K, yielding $C = 0.587(4)$ emu·K·mol^{-1}, and the asymptotic Weiss constant $\theta_P = -36(1)$K (figure 6a). The observed effective moment $\mu_{\text{eff}} = 2.167\mu_B$ for the title compound is in agreement with the predicted value of $1.732\mu_B$ for Cu^{2+} with $3d = 9$ ($S = 1/2$). The best fit (solid line marked χT in figure 6b) yielded an exchange parameter $J = -36.8(8)$ cm^{-1} at an effective g value of 2.0 for Cu^{2+} ($3d^9$, $S = 1/2$) using a formula of isolated octahedra aligned in a chain with the agreement factor of 5.8×10^{-4}.[55] Moderate antiferromagnetic (AF) Cu–Cu interactions are expected to predominate in the compound, which explains the negative Weiss temperature and interaction parameters, as observed. It is interesting to note that the interaction parameter (absolute value) for the
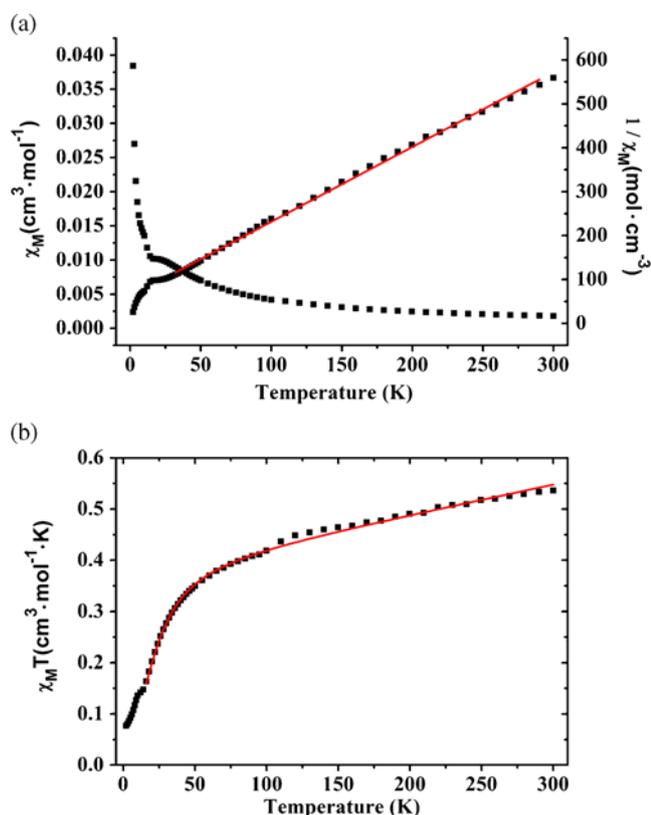
Figure 6. Temperature dependence of the molar magnetic susceptibility $\chi_M(T)$, inverse molar magnetic susceptibility $\chi_M^{-1}(T)$, and $\chi_M T$ of $(C_{12}H_{20}N_2)[CuCl_4]$ for an external field of 1000 Oe.

long distance of Cu-Cu at 6.75 Å is markedly larger than the analogous value ($J = -1.097\,\mathrm{cm^{-1}}$) in Fe-Fe with distance at 4.98 Å.[56] As discussed above, $[CuCl_4]$ in the crystal structure adopts an intermediate form between tetrahedral and square planar. This is probably attributable to the fact that the local environment of the $[CuCl_4]$ in the title compound is significantly distorted due to the presence of the Jahn-Teller ion Cu^{2+}, $3d^9$ (configuration: $(t_{2g})^6(d_{z2})^2(d_{x2-y2})^1$), whereas Fe^{3+} ($3d^5$) octahedron has degenerate orbitals. Correspondingly, the $\chi_M T$ values (figure 6b) decrease steadily from $0.534\,\mathrm{cm^3\,K\,mol^{-1}}$ at room temperature to $0.077\,\mathrm{cm^3\,K\,mol^{-1}}$ (per formula) at 2 K, conforming to the AF couplings. The moderate antiferromagnetic interactions are most likely propagated along the direction (nearly [111]) of the shortest linkage of Cu-Cu through the pathway of Cu-Cl_2-H-N-H-Cl_2-Cu ($d_{Cu-Cu} = 6.75$ Å, $d_{Cu-N} = 4.35$ or 4.22 Å, $\angle$Cu-N-Cu=103.9°).

4. Conclusions

In this report, a new hybrid compound, $(C_{12}H_{20}N_2)[CuCl_4]$, was synthesized as single crystals at room temperature and characterized by X-ray diffraction, IR spectroscopy and magnetic measurements. In the atomic arrangement of the title compound, the geometry of the tetra-coordinated Cu(II) ion is intermediate between tetrahedral and square planar geometry. Tetrachlorocuprate anions and piperazine-1,4-dium cations are connected together by N-H...Cl and C-H...Cl hydrogen bonds causing the formation of a 1-D hybrid chain running along the *a*-axis direction. The piperazinedium ring adopts the most stable chair conformation. The vibrational absorption bands were identified by infrared spectroscopy. Moderate antiferromagnetic Cu–Cu interactions in the compound are most probably attributable to the unusual geometry of $[CuCl_4]$.

Supplementary Information (SI)

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 1407713. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: Fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac

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