Tetrahedral Clusters of Copper(II): Crystal Structures and Magnetic Properties of $Cu_2Te_2O_5X_2$ (X = Cl, Br)

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The isostructural compounds of general formula $Cu_2Te_2O_5X_2$ (X = Cl, Br) have been synthesized by chemical transport reaction. They crystallize in the tetragonal system, space group $P\bar{4}$ with $a = 7.6209(3)$ Å, $c = 6.3200(4)$ Å, and $a = 7.8355(2)$ Å, $c = 6.3785(2)$ Å for $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ respectively. The three-dimensional network is built up by tetrahedral clusters of copper(II) in distorted square planar coordination, isolated in the [100] and [010] directions by $[Te_2O_5E_2]$ groups and in the [001] direction by $[TeO_3E]$ tetrahedra. This leads to what can be described as spin tubes in the [001] direction surrounded by large tunnels where $5s^2$ tellurium(IV) lone pairs and chlorine and bromine atoms interact. A careful analysis of the temperature dependence of the susceptibility reveals that even from the magnetic point of view, the building bricks are tetrahedra with all couplings roughly equivalent, and not squares with small diagonal couplings. These systems are thus expected to have very interesting magnetic properties, including a large singlet−triplet gap, and a band of singlet states inside this gap.

Introduction

During the past few years, a better understanding of the magnetic properties of low dimensional quantum spin systems has been the result of the synthesis of an increasing number of compounds suitable to test theoretical predictions. Compounds containing copper(II) and more recently vanadium(IV) have been extensively studied because they present a large variety of low dimensional quantum spin phenomena.[1−3] One approach to finding new compounds was simply based on topological considerations aiming at selecting structurally related compounds. This has proven to be effective, particularly, in the case of sodium−vanadium−oxygen systems with the discovery of two interesting phases $Na_{1.286}V_2O_5$[4] and $Na_2V_3O_7$,[5] the former formed by infinite stair like double strings of VO_5 square pyramids, whereas vanadium(IV) oxide nanotubes are present in the latter.

A more hypothetical approach that has been considered is to use the so-called lone pair cations which act as "structural scissors". Examples of such cations are As(III), Se(IV), Sn(II), Te(IV), Pb(II), Sb(III), and Bi(III). Interesting, but structurally complicated compounds have been obtained in the system $CuO-CuCl_2-SeO_2$: e.g. $Cu_9O_2(SeO_3)_4Cl_6$[6] and $Cu_3(SeO_3)_2Cl_2$[7] and two new forms of copper(II) vanadyl(IV) diselenite $CuVO(SeO_3)_2$ have been synthesized in the ternary diagram of $CuO-VO_2-SeO_2$.[8] Recent attempts to synthesize new low dimensional quantum phases in the system $CuO-CuCl_2-TeO_2$ resulted in the discovery of two compounds with the general formula $Cu_2Te_2O_5X_2$ (X = Cl, Br) which possess unique tetrahedral clusters of copper(II). In this paper we present the synthesis and crystal structure of these compounds. In addition, a preliminary analysis of their magnetic properties is reported.

Experimental Section

Single crystals of $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ were obtained from chemical transport reactions in sealed evacuated glass tubes using the method described by Bastide et al.[6] As starting materials CuO (Avocado Research Chemicals Ltd., 99+%), $CuCl_2$ (Avocado Research Chemicals Ltd., 98+%), $CuBr_2$ (Mallanckrodt Chemical Works, 99+%), and TeO_2 (Strem Chemicals, 99+%) were used. The preparation of $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ crystals were made from a mixture

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of CuO:CuX_2:TeO_2 (X = Cl, Br) in a molar ratio 4:2:3 at 450 and 440 °C, respectively, for 90 h. The synthesis products were characterized in a scanning electron microscope (SEM, JEOL 820) with an energy-dispersive spectrometer (EDS, LINK AN10000).

The synthesis products were a mixture of green $Cu_2Te_2O_5Cl_2$ or $Cu_2Te_2O_5Br_2$ crystals and brown crystals of unknown composition. For the magnetic susceptibility measurements monophasic powders of $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ were prepared in the stoichiometric molar ratio, CuO:CuX_2:TeO_2 = 1:1:2 (X = Cl, Br). The same synthesis temperatures and reaction times were used as for the single-crystal preparation. Before performing magnetic susceptibility measurements, the compounds were characterized by X-ray powder diffraction (XRD) obtained in a Guinier−Hägg focusing camera with subtraction geometry. Cu Ka_1 radiation ($\lambda = 1.54060$ Å) was used, and silicon, $a = 5.430880(35)$ Å, was added as internal standard. The recorded films were evaluated in an automatic film scanner.

The single-crystal X-ray data were collected on a Bruker-AXS SMART2K CCD diffractometer equipped with an Oxford Cryostream crystal cooling system. In excess of half a reflection sphere were collected by means of 0.3° ω scans. The data were collected and reduced using SMART and SAINT.[9] Gaussian face indexing absorption correction, structure solution, refinement and graphical illustrations were made with SHELXTL.[10] Crystal data for both phases are reported in Table 1. The susceptibility measurements were performed using a SQUID magnetometer MPMS-5 Quantum Design in a sweep two-temperature mode (1 K/min, acquisition every 2 deg). The magnetic field intensity was 1 kG. Diamagnetic corrections were made.

Results and Discussion

Crystal Structure. $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$ are isostructural and crystallize in the tetragonal system, space group $P\bar{4}$. Experimental parameters, atomic coordinates, and selected interatomic distances are listed in Tables 1, 2, and 3, respectively. The copper atom is coordinated to three oxygen atoms and one chlorine or bromine atom creating a somewhat distorted square plane. The peculiarity of this structure type arises from the way these square planes are connected with respect to one another. This arrangement is presented in Figure 1a, showing four square planes linked via the oxygen atom O1 forming clusters of the formula $[Cu_4O_8X_4]_n$. Because of the inversion axis, $\bar{4}$, these clusters are not flat, as two copper atoms are located at z and two at $-z$. They thus form a distorted tetrahedron represented in Figure 1b, with copper(II) located at the same height, $Cu-Cu^{iii}$ with distances 3.591(2) and 3.543(3) Å, and those located at the second height, $Cu-Cu^{i}$ with distances of 3.229(2) and 3.196(2) Å, for the chlorine and bromine compounds, respectively.

The tellurium atoms exhibit a classical coordination polyhedron, classically noted $[TeO_3E]$, formed by three oxygen atoms with Te−O distances ranging between 1.87 and 1.94 Å, and the $5s^2$ lone pairs (E). Two $[TeO_3E]$ tetrahedra are linked via oxygen atom O3 to form $[Te_2O_5E_2]$ groups, establishing, as represented in Figure 2, a three-dimensional network by isolating the copper(II) clusters in the [100] and [010] directions. In the [001] direction clusters are linked together via only one $[TeO_3E]$ tetrahedron leading to what can be seen as spin columns parallel to the z axis. The tellurium lone pairs point into the large voids located around these columns, interacting with the chlorine or bromine atoms. This kind of interaction appears to be a common feature in

Table 1. Crystal Data and Structure Refinement for $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$

empirical formula	$Cu_2Te_2O_5Cl_2$	$Cu_2Te_2O_5Br_2$
formula weight	533.18	622.10
temperature	223(2) K	223(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system	tetragonal	tetragonal
space group	$P\bar{4}$	$P\bar{4}$
unit cell dimensions	$a = 7.6209(3)$ Å $c = 6.3200(4)$ Å	$a = 7.8355(2)$ Å $c = 6.3785(2)$ Å
volume	367.05(3) Å^3	391.61(2) Å^3
Z	2	2
density (calculated)	4.824 mg/m^3	5.276 mg/m^3
absorption coefficient	14.275 mm^{-1}	22.902 mm^{-1}
absorption correction	Gaussian face indexed	Gaussian face indexed
transmission min/max	0.1193/0.5010	0.1057/0.4566
$F(000)$	472	544
crystal color	green	green
crystal habit	needle	needle
crystal size	0.325 × 0.688 × 0.050 mm^3	0.255 × 0.044 × 0.038 mm^3
θ range for data collection	2.67−32.68°	2.60−32.68°
index ranges	$-11 \le h \le 11$ $-11 \le k \le 10$ $-9 \le l \le 7$	$-10 \le h \le 11$ $-7 \le k \le 11$ $-9 \le l \le 9$
reflections collected	3518	3801
independent reflections	1255 [R(int) = 0.0194]	1353 [R(int) = 0.0186]
completeness to $\theta = 32.68°$	96.2%	95.9%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	1255/0/53	1353/0/53
goodness-of-fit on F^2	1.345	1.193
final R indices [$I > 2\sigma(I)$]	R1 = 0.0203 wR2 = 0.0450	R1 = 0.0159 wR2 = 0.0332
R indices (all data)	R1 = 0.0214 wR2 = 0.0452	R1 = 0.0183 wR2 = 0.0334
absolute structure parameter	0.14(3)	0.484(10)
extinction coefficient	0.0132(8)	0.0100(4)
largest diff. peak and hole	0.979 and −0.844 e Å^{-3}	0.856 and −0.864 e Å^{-3}

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $Cu_2Te_2O_5Cl_2$ (top) and $Cu_2Te_2O_5Br_2$ (bottom)

	x	y	z	U(eq)[a]
Te	6481(1)	8291(1)	3565(1)	10(1)
Cu	7309(1)	4531(1)	1579(1)	11(1)
Cl	9078(2)	2222(2)	1879(2)	19(1)
O(1)	5858(4)	6675(3)	1408(6)	12(1)
O(2)	4718(4)	7713(4)	5516(5)	14(1)
O(3)	5000	10000	2157(8)	17(1)
		(suite)		
Te	6379(1)	8210(1)	3615(1)	8(1)
Cu	7228(1)	4617(1)	1555(1)	10(1)
Br	9169(1)	2302(1)	1842(1)	18(1)
O(1)	5704(3)	6683(3)	1425(4)	11(1)
O(2)	4684(3)	7590(3)	5558(4)	12(1)
O(3)	5000	10000	2389(5)	14(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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(9) Bruker-AXS. SMART and SAINT. Area Detector Control and Integration Software.; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1998.

(10) Bruker AXS. SHELXTL version 5.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

Table 3. Bond Lengths (Å) and Angles (deg) for $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$[a]

X = Cl, Br	$Cu_2Te_2O_5Cl_2$	$Cu_2Te_2O_5Br_2$
Te−O(2)	1.876(3)	1.881(2)
Te−O(1)	1.897(3)	1.914(3)
Te−O(3)	1.940(2)	1.936(1)
Cu−O(2)^{i}	1.948(3)	1.942(2)
Cu−O(1)^{i}	1.971(4)	1.964(3)
Cu−O(1)	1.976(3)	2.013(2)
Cu-X	2.225(1)	2.374(6)
Cu−Cu^{iii}	3.591(2)	3.543(3)
Cu−Cu^{i}	3.229(2)	3.196(2)
O(2)−Te−O(1)	98.09(14)	97.11(11)
O(2)−Te−O(3)	92.42(14)	93.39(10)
O(1)−Te−O(3)	87.73(14)	90.22(10)
O(2)^{i}-Cu−O(1)^{i}	170.35(12)	170.18(10)
O(2)^{i}-Cu−O(1)	84.09(13)	84.18(11)
O(1)^{i}-Cu−O(1)	86.27(14)	86.22(11)
O(2)^{i}-Cu-X	93.22(10)	92.82(8)
O(1)^{i}-Cu−X	96.38(9)	96.66(7)
O(1)−Cu−X	176.21(9)	175.89(7)
Te−O(1)−Cu^{ii}	124.54(14)	127.27(12)
Te−O(1)−Cu	110.92(16)	107.99(12)
Cu^{ii}-O(1)−Cu	109.82(16)	106.89(12)
Te−O(2)−Cu^{iv}	116.50(15)	117.58(13)

[a] Symmetry transformations used to generate equivalent atoms: (i) $y, -x + 1, -z$; (ii) $-y + 1, x, -z$; (iii) $-x + 1, -y + 1, z$; (iv) $-y + 1, x, -z + 1$.

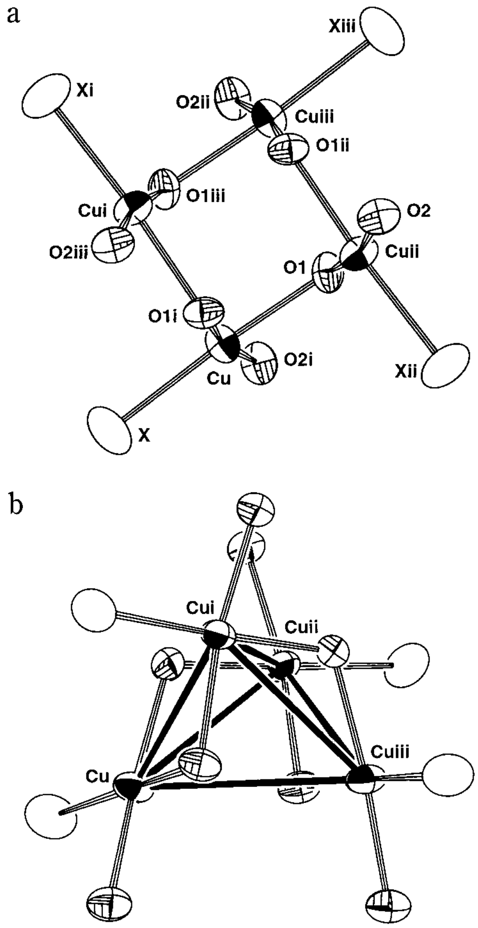

Figure 1. Ortep drawings of (a) an isolated cluster of four $[CuO_3X]$ square planes viewed down the z axis; (b) the same cluster as in (a) but tilted to show the tetrahedral arrangement of copper(II) ions.

systems involving lone pair elements such as oxochlorides, with the shortest distances E-Cl/Br being 2.62 and 2.675 Å respectively, slightly longer than those seen in $Cu_3(SeO_3)_2Cl_2$,[7] Francisite $Cu_3Bi(SeO_3)_2O_2Cl$,[11] and $Cu_5O_2(SeO_3)_2Cl_2$[12] which are in the range 2.10−2.51 Å.

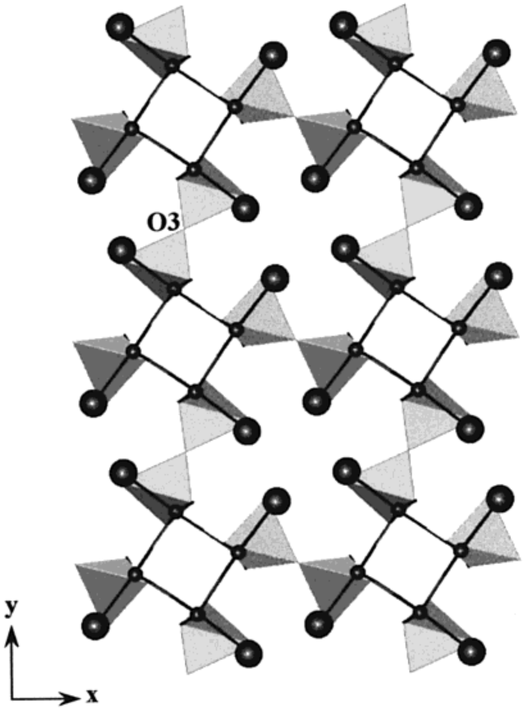

Figure 2. Projection of $Cu_2Te_2O_5X_2$ (X = Cl, Br) onto the (001) plane. The big and small spheres are halogenide and copper atoms, respectively. Cu−O bonds are represented by sticks and for the sake of clarity the oxygen atoms are not drawn. $[TeO_3E]$ tetrahedra are in gray.

Magnetic Properties. The magnetic susceptibility of both systems is characteristic of spin gap systems with a well-pronounced maximum and a very rapid decrease at low temperature. This is particularly clear for $Cu_2Te_2O_5Br_2$. As usual, it is difficult to extract the gap from such macroscopic measurements because of the contribution of paramagnetic impurities at very low temperature. In the present case, we do not have points at low enough temperature to perform a reliable extraction, and a direct determination of the gap will have to wait until experiments that are not sensitive to paramagnetic impurities, for instance NMR, are reported. It is nevertheless possible to extract physical information from the intermediate and high-temperature range. Given the structure of the system, the dominant coupling will be between the spins of a tetrahedron. So, we have tried to fit the susceptibility by assuming that the system is a collection of independent tetrahedra. Since there are two types of bonds a priori, we have used a Heisenberg model including two exchange integrals, J_1 between nearest-neighbors, J_2 between next-nearest neighbors:

$$H = J_1(\vec{S}_1\vec{S}_2 + \vec{S}_2\vec{S}_3 + \vec{S}_3\vec{S}_4 + \vec{S}_4\vec{S}_1) + J_2(\vec{S}_1\vec{S}_3 + \vec{S}_2\vec{S}_4) \quad (1)$$

This Hamiltonian has the remarkable property that it

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(11) Pring, A.; Gatehouse, B. M.; Birch, W. D. *Am. Mineral.* **1990**, *75*, 1421.

(12) Galy, J.; Bonnet, J. J.; Andersson, S. *Acta Chem. Scand.* **1979**, *A33*, 383.

can be reexpressed entirely in terms of $\vec{S}_{13} \equiv \vec{S}_1 + \vec{S}_3$, $\vec{S}_{24} \equiv \vec{S}_2 + \vec{S}_4$, and $\vec{S}_{\mathrm{tot}} = \vec{S}_{13} + \vec{S}_{24}$ as

$$H = \frac{J_1}{2}(\vec{S}_{\mathrm{tot}}^{\;2} - \vec{S}_{13}^{\;2} - \vec{S}_{24}^{\;2}) + \frac{J_2}{2}(\vec{S}_{13}^{\;2} - \vec{S}_{24}^{\;2} - 3) \quad (2)$$

By using standard rules for the addition of angular momenta, one can easily get the spectrum, hence the susceptibility. For one site, it is given by

$$\chi(T) = \frac{(g\mu_\beta)^2}{4}\chi(J_1,J_2;T) \quad (3)$$

with

$$\chi(J_1,J_2;T) = \beta[2\exp(-\beta J_1) + 4\exp(-2\beta J_1 + \beta J_2) + 10\exp(-3\beta J_1)]/[1 + 3\exp(-\beta J_1) + \exp(-2\beta J_1 + 2\beta J_2) + 6\exp(-2\beta J_1 + \beta J_2) + 5\exp(-3\beta J_1)] \quad (4)$$

with $\beta = 1/k_\mathrm{B}T$. This formula is actually equivalent to a formula to be found in ref 13 with the changes $J_1 \rightarrow -J'$ and $J_2 \rightarrow -J$.

In both cases, a very good fit down to temperatures below the maximum could be achieved. The experimental points below the temperature where the fitting curve ends have not been included in the fit. In both cases, the relative error of the sum of squares was less than 10^{-5}. The parameters of the fits are given in the figures. Since there are two Cu per unit cell, the constant C would be equal to 0.75 in these units if the g factor was equal to 2. The g factor are thus given by 2.08 and 2.15 for $Cu_2Te_2O_5Cl_2$ and $Cu_2Te_2O_5Br_2$, respectively. This values are typical for Cu^{2+} in this kind of environment. Accordingly, one expects the van Vleck susceptibility to be almost twice as large for $Cu_2Te_2O_5Br_2$ than for $Cu_2Te_2O_5Cl_2$, in agreement with the values 5.3×10^{-4} and 3.1×10^{-4} deduced from our fit. It turns out that the best fit is obtained in both cases when $J_1 = J_2$ (see Figures 4 and 5) with $J_1 \cong 38.5$ K for $Cu_2Te_2O_5Cl_2$ and $J_1 \cong 43$ K for $Cu_2Te_2O_5Br_2$. Since the bonds are inequivalent, this result is rather unexpected. In fact, one would naively expect J_1 to be much larger than J_2 since there is an oxygen between nearest neighbors but not between next-nearest neighbors. It turns out that the condition $J_2/J_1 = 1$ is necessary to reproduce at the same time the high-temperature regime and the position of the maximum. In particular, it is *not* possible to fit the data in the whole temperature range if $J_2/J_1 \ll 1$.

Since the fits were performed without any coupling between the tetrahedra, the precise value of the ratio $J_2/J_1 = 1$ should not be taken too literally. While this coupling between tetrahedra enters the Curie−Weiss temperature to first order, it will modify the singlet−triplet gap, hence the position of the maximum, only to second order. So, the condition $J_2/J_1 = 1$ will be somehow relaxed by taking into account the coupling between tetrahedra. Still, given the accuracy of the fits obtained without these extra couplings, they are presumably very small, which is logical from the point of view of quantum chemistry given the distance between Cu atoms of neighboring tetrahedra. So we are presumably in the region $J_2/J_1 \cong 1$. This is consistent with the fact that the Cu atoms form almost perfect tetrahedra as long as the exchange is not taking place through the O atoms.

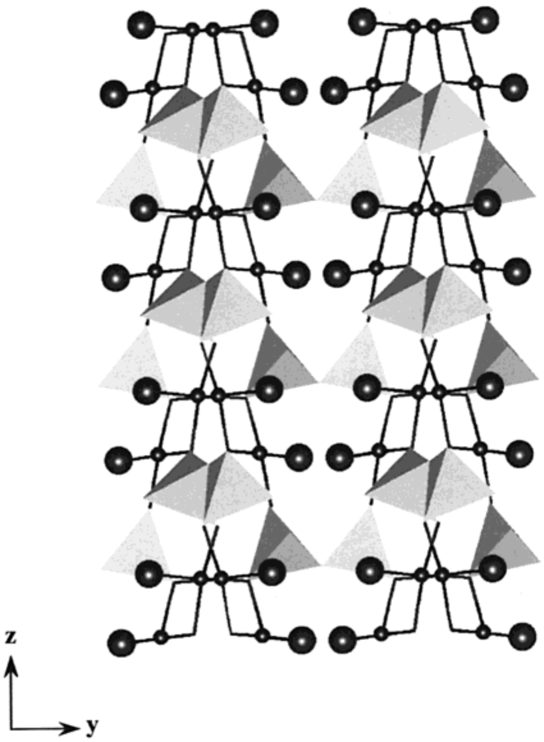

Figure 3. Projection of $Cu_2Te_2O_5X_2$ (X = Cl, Br) onto the (100) plane.

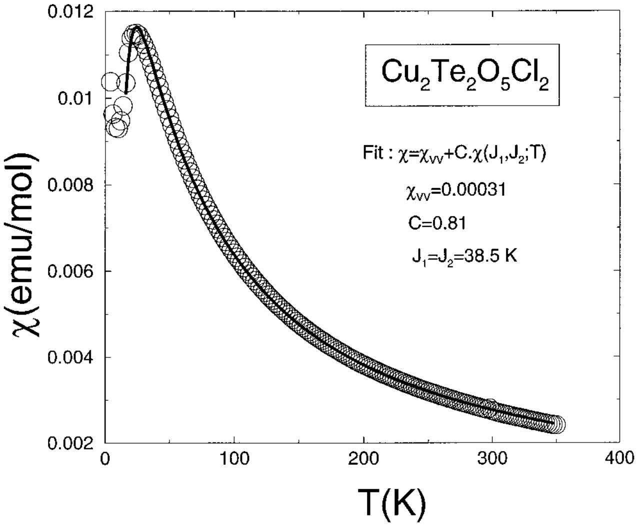

Figure 4. Magnetic susceptibility of $Cu_2Te_2O_5Cl_2$ (open circles) fit using eq 1, solid line.

The physical consequences of this property are remarkable. The ground state of a cluster of four spins described by eq 1 is always a singlet. The first excited state, however, can be a singlet or a triplet depending on the relative value of J_1 and J_2: If $J_2 < J_1/2$ or $J_2 > 2J_1$ the first excitation is a triplet. This is in particular the case if J_2 is very small. But if $J_1/2 \leq J_2 \leq 2J_1$ the first excitation is a singlet, and the singlet−singlet gap Δ_{SS} is given by $\Delta_{SS} = 2|J_2 - J_1|$. When $J_2 = J_1$, the singlet−triplet gap Δ_{ST} is equal to J_1. So, if $J_2 \cong J_1$, we expect to find a lot of low-lying singlets below the

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(13) Kahn, O. *Molecular Magnetism*; VCH publishers: New York, 1993; p 238.

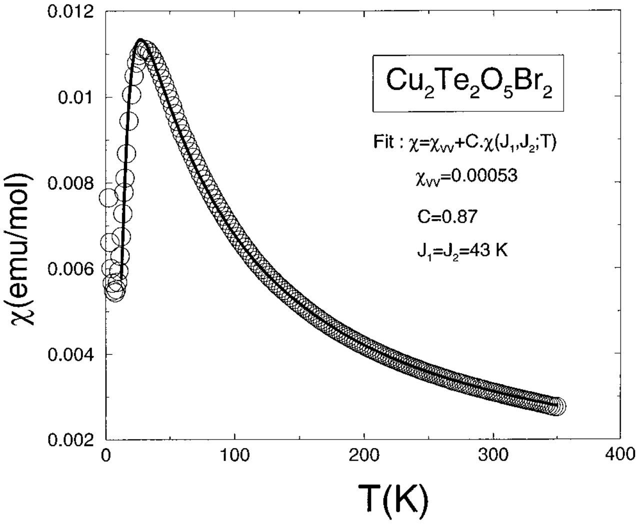

Figure 5. Magnetic susceptibility of $Cu_2Te_2O_5Br_2$ (open circles) fit using eq 1, solid line.

singlet−triplet gap, their number being equal to $2^{N/4}$, where N is equal to the number of Cu sites. The coupling between the tetrahedra will remove the degeneracy between these singlet excitations and will create a band, but as long as the coupling between the tetrahedra is small compared to J_1, this picture will remain valid. This feature is reminiscent of the properties of strongly frustrated systems, like the *Kagomé* antiferromagnet, for which extensive numerical simulations have revealed the presence of an exponential number of low lying singlets,[14] as well as those of a one-dimensional model of coupled tetrahedra.[15] The presence of a large singlet−triplet gap Δ_{ST} for all values of J_2/J_1 implies that the magnetic susceptibility will behave like $e^{-\Delta_{ST}/T}$ at low temperature, in agreement with the results reported in this paper. However, the singlets will influence the low-temperature specific heat, which will have a spin contribution even at temperatures much lower than Δ_{ST}, and they will appear as separate excitations below Δ_{ST} in spectroscopic methods that are sensitive to singlet excitations, like for instance Raman spectroscopy.

Conclusions

Two new isostructural compounds in the system $CuO-CuX_2-TeO_2$ ($X = Cl, Br$) have been synthesized by chemical transport reaction. The compounds have the general formula $Cu_2Te_2O_5X_2$ ($X = Cl, Br$). The copper atom is coordinated to three oxygen atoms and one halogen atom in a slightly distorted square-planar coordination. The unique feature with the new structures is that the square planes are connected so that they form units with the formula $[Cu_4O_8X]_n$. These units are not flat but are arranged so that they show unique tetrahedral clusters of copper(II). The tellurium atoms exhibit a classical coordination polyhedron formed by three oxygen atoms and the $5s^2$ lone pairs. The $[TeO_3E]$ tetrahedra are linked so that they isolate the copper(II) clusters. The tellurium lone pairs point into large voids in the structures where they interact with the chlorine or bromine atoms. A preliminary analysis of the magnetic properties is reported. The temperature dependence of the magnetic susceptibility is measured for both phases and an attempt is made to fit the calculated susceptibility by assuming that the system is a collection of independent copper(II) tetrahedra.

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