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$Cu_4(AsO_4)_2(O)$: A New Copper Arsenate with Unusual Low Temperature Magnetic Properties

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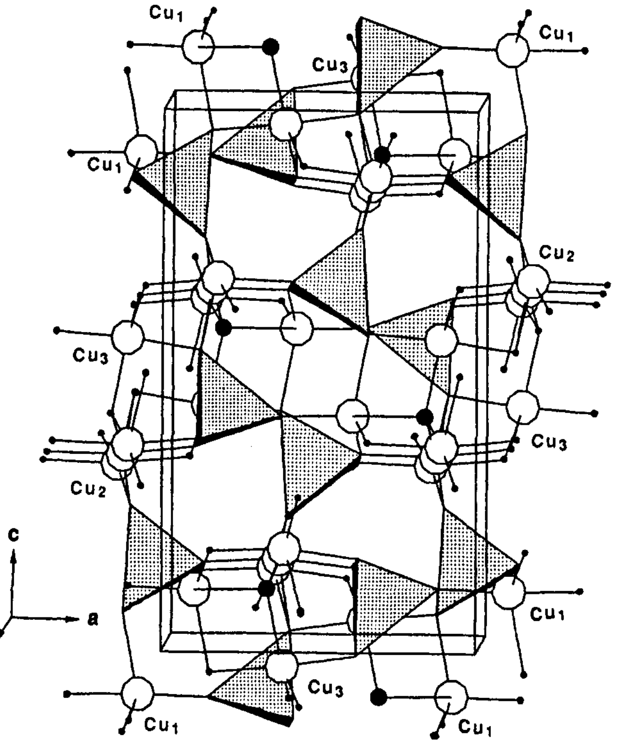

Figure 1. A drawing of the unit cell contents of the structure of $Cu_4(AsO_4)_2O$. AsO_4 tetrahedra are represented by the shaded polyhedra. The μ_4-oxide ions O(6) are represented by the large black spheres. The nearest neighbor contacts to the copper ions (large circles) are indicated by lines. Selected copper ions have been labeled. Small black spheres are oxygen atoms of incomplete AsO tetrahedra. Interatomic distances (Å) and angles (°) about the oxide ion O(6) are as follows: Cu(1)−O(6) = 1.907(6), Cu(2)−O(6) = 1.912(6), Cu(3)−O(6) = 2.004(7); Cu(1)−O(6)−Cu(2) = 101.5(2), Cu(1)−O(6)−Cu(2′) = 101.5(2), Cu(1)−O(6)−Cu(3) = 101.5(3), Cu(2)−O(6)−Cu(2′) = 118.8(3), Cu(2)−O(6)−Cu(3) = 114.8(2), Cu(2′)−O(6)−Cu(3) = 114.8(2).

Low dimensional materials having anisotropic transport and magnetic properties have been the source of great interest and potentially great importance.[1] Efforts to synthesize these materials have recently attracted considerable attention.[2] We now report the preparation, structural characterization, and magnetic properties of a new copper oxide arsenate: $Cu_4(AsO_4)_2O$, **1**. Copper arsenate occurs naturally in the form of the mineral lammerite, $Cu_3(AsO_4)_2$.[3] A synthetic polymorph $Cu_3(AsO_4)_2$ is also known.[4] $Cu_4(AsO_4)_2O$ was obtained as transparent dark green crystals from the reaction of CuO with $As_2O_5{\cdot}xH_2O$ in a $BaCO_3$ flux at 1090 °C for 72 h.[5,6] $Cu_4(AsO_4)_2O$ could be imagined as a composite of $Cu_3(AsO_4)_2$ and CuO, but a three dimensional structural analysis shows that it is an intimate blend of the two and a truly new material.[8] A view of the crystallographic unit cell is shown in Figure 1. The structure contains three independent copper ions. Two of these possess distorted trigonal bipyramidal geometries formed by arrangements of five oxygen atoms derived from the arsenate ions and the one "free" oxide ion, O(6). The third copper ion exhibits a distorted square pyramidal CuO_5 geometry. There is one "free" oxide ion that is surrounded by four copper ions in a distorted tetrahedral arrangement, **A**. Three of the copper ions are bridged by the tripodal base of a single $[AsO_4]^{3-}$ ion. The $Cu_4(\mu_4\text{-}O)$ structural motif has been observed in a number of tetracopper coordination complexes (e. g. $[Cu_4(\mu_4\text{-}O)Cl_{10}]^{4-}$ and $Cu(\mu_4\text{-}O)X_6L_4$, X = Cl, Br; L = py, DMSO, PR_3, etc.)

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(6) A mixture of 0.4748 g (2.406 mmol) of $BaCO_3$, 0.6690 g (8.409mmol) of CuO, and 0.9570 g (3.600 mmol) of $As_2O_5{\cdot}H_2O$ was ground thoroughly in a mortar and then transferred to a ceramic crucible. The crucible was then placed in the oven (Thermolyne Model F21125) and heated in air to 1090 °C for 72 h. After the heating period, the oven was cooled slowly (approximately 1°C/min) to 600 °C, and then cooled rapidly to room temperature. A dark green transparent platelet was cleaved from the bulk sample and analyzed by single-crystal X-ray diffractometry. The yield is estimated to be 20−30%. Other components in this mixture have not yet been fully identified. It is notable that this green product was not obtained when stoichiometric quantities of CuO, and $As_2O_5{\cdot}xH_2O$ were heated to 1090 °C in the absence of $BaCO_3$. The percent Cu/As elemental composition was obtained on a single crystal by scanning electron microscopy. Anal. Cu/As: % calcd, 46.4/27.3; (% found, 45.3/29.4) assuming the remaining material is oxygen.

(7) There is a brief report of a compound formulated as $Cu_4(As_2O_7)O_2$,[7] but not structurally characterized. This does not appear to be the same as the compound that we are reporting because of substantial differences between the observed and predicted powder patterns of these compounds.

(8) For $Cu_4(AsO_4)_2O$: crystal system: orthorhombic; space group = *Pnma*, $a = 8.253(1)$ Å, $b = 6.4122(8)$ Å, $c = 13.789(3)$ Å, $Z = 4$, 939 reflections ($I > 3.0\sigma(I)$), $R = 0.038$. Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An empirical absorption correction (based on three azimuthal ψ scans) was applied to the data.

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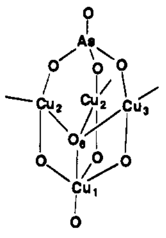
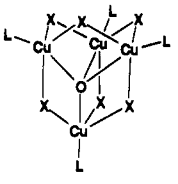
which contain an oxide ligand tetrahedrally surrounded by four copper ions, **B**.[9] The copper ions form extended two dimensional layers via a network of Cu−O−Cu bridges. The layers are interconnected via Cu−O −As−O−Cu bridging units involving the arsenate ions.



A



B

Magnetic susceptibility measurements on **1** show that it is paramagnetic with an effective magnetic moment, μ_{eff}, of 1.95 μ_B (Bohr magnetons) at 280 K.[10] This value is typical of copper(II) ions having one unpaired electron.[9a] The existence of antiferromagnetic coupling of the unpaired electrons was demonstrated by a progressive decrease in the χT product as the temperature was reduced. Similar antiferromagnetic behavior has been observed for the $Cu_4(\mu_4\text{-}O)$ complexes **B** in the solid state;[9a,b,11] however, at very low temperatures there is a sharp increase in the χT product which is characteristic of an ordered magnetic state. This has not been observed previously for the $Cu_4(\mu_4\text{-}O)$ complexes. This is represented by a narrow maximum in χT plot in the range 5−25K[10] and can be attributed to long-range spin interactions provided by the bridging AsO_4 groups. Similar behavior has been observed in other low dimensional solid state magnetic materials.[12] Further support for an ordered low temperature magnetic state was provided by isothermal magnetization measurements recorded at 5 K.[11] The magnetization was observed to increase rapidly as the field strength was increased from 0−200 Oe. This was followed by a slow and progressive increase over the range 200−50 000 Oe. Further studies are in progress.

Supporting Information Available: A plot of the magnetic susceptibility product χT vs T for **1** measured at 5 kOe in the range 2−300K, a plot of the magnetization of **1** (μ_B/Cu atom) vs magnetic field strength H = 0−50 000 (Oe) at 5 K, tables of crystal data and experimental data, positional parameters, interatomic distances and angles, and anisotropic thermal parameters, and text detailing the structure determination and magnetic measurements (8 pages). Ordering information is given on any current masthead page.

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(10) Magnetic measurements were performed on a Quantum Design SQUID magnetometer using a polycrystalline sample of 1.45 mg of carefully hand selected pure green crystals. This sample was first cooled down to 5 K in the absence and of an applied field and then measured upon warming in a static field of 5 kOe. The data were corrected for sample holder contribution and for core diamagnetism (χ_{dia} was taken equal to -176.10^{-6} emu/mol using the Pascal's constants). The mean room temperature magnetic moment is μ_{eff} = 1.95 B. M./Cu. The plot of χT vs T shows an approximately linear decrease of χT with T in the temperature range 30−300 K which is consistent with antiferromagnetic coupling. At about 25 K a sharp increase in χT is observed which reaches a maximum at about 20 K. This followed by a sharp decrease which continues to the lowest recorded temperature, 5K. The magnetization M (μ_B/Cu atom) vs H (Oe) at 5 K shows a rapid increase in M in the range 0−200H (Oe) followed by a slow increase in the range 200−50 000 Oe. Plots of the magnetic behavior of $Cu_4(AsO_4)_2O$ (**1**), χT vs T measured at 5 kOe in the range 2−300 K, and (2) magnetization (μ_B/Cu atom) vs H (Oe) at 5 K have been deposited; see Supporting Information.

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