The Synthesis, Crystal Structures and Magnetic Properties of $Cu_4(AsO_4)_2(O)$ and $Ba_2Cu_7(AsO_4)_6$

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Two new compounds $Cu_4(AsO_4)_2O$ (**1**) and $Ba_2Cu_7As_6O_{24}$ (**2**) were obtained from a mixture of CuO and $As_2O_5 \cdot xH_2O$ heated to 1090°C for 72 h in a $BaCO_3$ flux. Compound **1** was obtained as dark green crystals, belonging to the orthorhombic crystal system. Compound **2** was obtained as light gray to colorless crystals belonging to the triclinic crystal system. The structure of **1** contains two copper ions with distorted trigonal bipyramidal geometries and a third with a distorted square pyramidal geometry. One "oxide" ion is surrounded by four copper ions in a distorted tetrahedral arrangement. Compound **2** consists of two chains with alternating units of trigonal bipyramidal CuO_5 and square planar CuO_4 units, with the oxygen atoms derived from the AsO_4 groups. Magnetic susceptibility measurements of **1** and **2** both show effective magnetic moments, $\mu_{eff} = 1.90-1.95$ B.M./Cu at 25°C, which is consistent with Cu^{2+} ions having one unpaired electron. Significant antiferromagnetic coupling was revealed by variable temperature measurements. At very low temperatures (15–25 K) samples of both **1** and **2** undergo a transition to a weak ferromagnetic state.

Low dimensional materials with anisotropic transport and anisotropic magnetic properties have been the source of great interest and importance[1-2]. Efforts to synthesize and study these materials have recently attracted considerable attention[2]. Materials containing layers of square planar copper oxide groupings have been shown to exhibit the property of superconductivity at unusually high temperatures[3]. We now report the preparation, structural characterization and magnetic properties of two new copper arsenates: $Cu_4(AsO_4)_2O$ (**1**) and $Ba_2Cu_7As_6O_{24}$ (**2**). Copper arsenate occurs naturally in the form of the mineral lammerite, $Cu_3(AsO_4)_2$[4]. A synthetic polymorph of $Cu_3(AsO_4)_2$ is also known[5]. A preliminary report on compound **1** has been published[6].

Results and Discussion

Dark green crystals of $Cu_4(AsO_4)_2O$ (**1**) were clearly visible in mixtures obtained from CuO and $As_2O_5 \cdot xH_2O$ heated to 1090°C in a $BaCO_3$ flux for 72 h. The structure of $Cu_4(AsO_4)_2O$ was obtained by a single-crystal x-ray diffraction analysis. A view of the crystallographic unit cell is shown in Figure 1. Selected interatomic distances for **1** are listed in Table 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. The "free" oxide ion has four copper ions in a slightly distorted tetrahedral arrangement **A** as its nearest neighbors: Cu(1)–O(6) = 1.907(6) Å, Cu(2)–O(6) = 1.912 (6) Å, Cu(3)–O(6) = 2.004(7) Å; 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)°. Three of these copper ions are further connected by the tripodal base of a single $[AsO_4]^{3-}$ ion. A similar structural motif has been observed in a number of tetracopper 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.) which have a central "oxide" ligand tetrahedrally surrounded by four copper ions, **B**[7].

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 bridges that contain arsenic atoms. There is a brief report of a compound formulated as $Cu_4(As_2O_7)O_2$[8], which was not structurally characterized. This does not appear to be the same as compound **1** since there are substantial differences between the observed and predicted X-ray powder patterns of these two compounds.

Magnetic susceptibility measurements of **1** show that it is paramagnetic with an effective magnetic moment, μ_{eff} = 1.95 B.M. at 280 K (using the formula $\mu_{eff}/\mu_B = (8\chi T)^{1/2}$ where χ is expressed in emu/Cu mol). This value is typical of copper(II) ions having one unpaired electron[7]. A plot of χT versus temperature for **1** is shown in Figure 2. The existence of antiferromagnetic coupling of the unpaired electrons was demonstrated by a progressive decrease in χT as the temperature is lowered. Antiferromagnetic behavior was also observed for the $Cu_4(\mu_4\text{-}O)$ complexes **B**[7,9]. Interestingly, at very low temperatures a sharp increase followed by a sharp decrease in χT vs. T was observed for **1** in the range 5–30 K; this is seen as a sharp peak in Figure 2 in

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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 solid black circles. The nearest neighbor contacts to the copper ions (large circles) are indicated by lines. Selected copper ions have been labeled

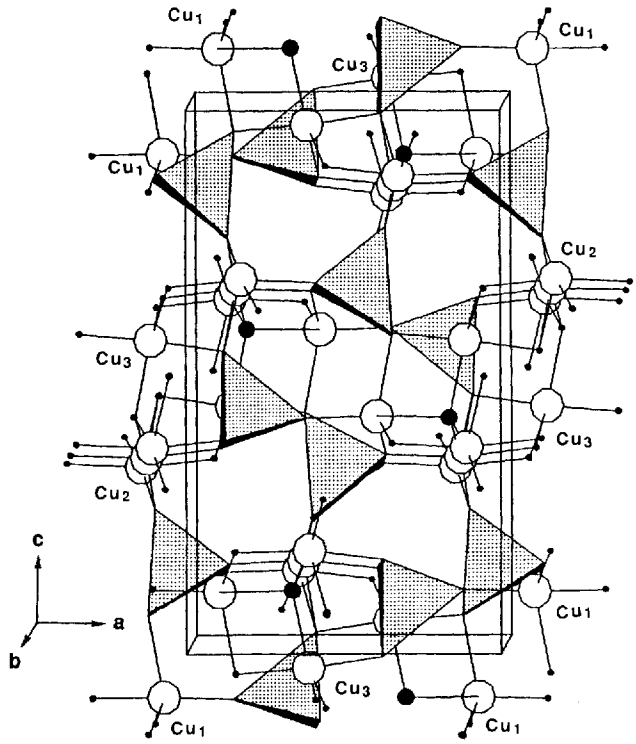
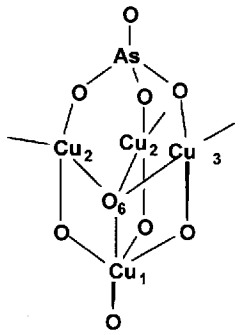


Table 1. Selected interatomic distances with esd's for $Cu_4(AsO_4)_2(O)$ (1)

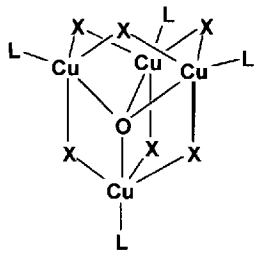
As(1)–O(2)	1.710(7)	Cu(1)–O(7)	1.843(7)
As(1)–O(4)	1.707(5)	Cu(2)–Cu(2')	3.120(2)
As(1)–O(4')	1.707(5)	Cu(2)–Cu(3)	3.133(1)
As(1)–O(7)	1.629(7)	Cu(2)–O(1)	1.974(5)
As(2)–O(1)	1.693(7)	Cu(2)–O(2)	2.338(6)
As(2)–O(3)	1.672(7)	Cu(2)–O(4)	1.955(4)
As(2)–O(5)	1.685(5)	Cu(2)–O(5)	1.973(4)
As(2)–O(5')	1.685(5)	Cu(2)–O(6)	1.912(3)
Cu(1)–Cu(2)	2.957(1)	Cu(3)–O(2)	1.954(6)
Cu(1)–Cu(3)	3.028(2)	Cu(3)–O(3)	1.921(6)
Cu(1)–O(3)	2.142(7)	Cu(3)–O(4)	2.182(5)
Cu(1)–O(5)	2.044(5)	Cu(3)–O(4')	2.182(5)
Cu(1)–O(5')	2.044(5)	Cu(3)–O(6)	2.004(7)
Cu(1)–O(6)	1.907(6)		

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

this temperature range. This can be interpreted in terms of a long-range ordering characteristic of a weak ferromagnetic state. Similar behavior has been observed in other low-dimensional solid-state magnetic materials[10]. A plot of the magnetization (magnetic moment/Cu atom) of **1** as a function of the field strength at 5 K is shown in Figure 3. There is a sharp increase in M between 0 and 100 Oe, which is followed by a slow progressive increase in M over the range 200–45000 Oe. The sharp increase is characteristic of the formation of a magnetically ordered state. Isothermal magnetization measurements at 200 K and 300 K were completely linear in the range 0–45000 Oe, indicating the absence of ordering and also the absense of impurities with ferro- or ferrimagnetism at these higher temperatures. Figure 4 shows a plot of the magnetic moment versus H when the field direction is applied and then reversed. There is a slight hysteresis observed at about 500 Oe, but the remanent moment is zero within experimental error. This behavior is expected for a weak ferromagnet; the low-field behavior corresponds to the saturation of the weak moment. By fitting the high-field data with the expression $\sigma_0 + A^*H$, one can extract a value for the saturated weak moment of σ_0 = 0.031 B.M./Cu atom. For a simple antiferromagnet, A is a constant which depends on the temperature and on the anisotropy and exchange fields. Spin canting could be responsible for the weak ferromagnetism[11]. A canting angle of 2° would produce a value of 0.03 B.M./Cu as observed.

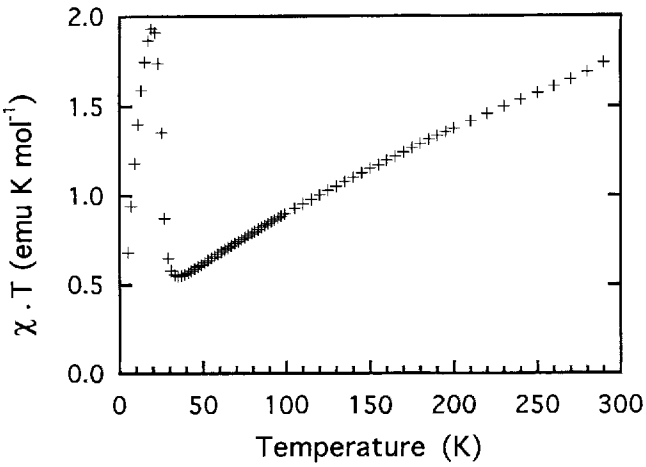


A



B

Figure 2. A plot of the magnetic susceptibility produet χT versus T for $Cu_4(AsO_4)_2O$ measured at 5 kOe in the range 2–300 K: A sharp maximum at ≈20 K shows the onset of the weak ferromagnetic response



In addition to the green crystals of **1**, small amounts of gray to colorless crystals could also be obtained from the heated mixtures of CuO, $As_2O_5 \cdot xH_2O$ and $BaCO_3$. These crystals were also characterized crystallographically. Selected interatomic distances for **2** are listed in Table 2. The formula established on the basis of this analysis is $Ba_2Cu_7As_6O_{24}$ (**2**). Compound **2** is isomorphous and isostructural with the recently reported compound $Pb_2Cu_7As_6O_{24}$[12]. The structure of **2** contains five independent copper atoms. Three of these lie on special positions (centers of sym-

Figure 3. A plot of the magnetization (magnetic moment/Cu atom) of **1** as a function of the field strength at 5 K: (O) for increasing field and (+) for decreasing field

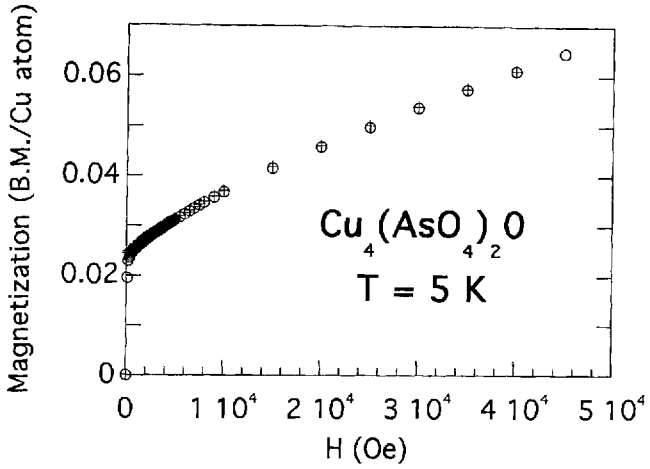
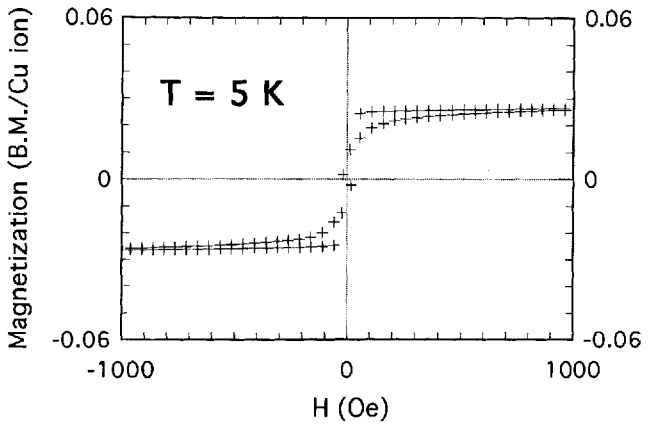


Figure 4. A plot of the magnetic moment (μ) versus H (Oe) of **1** at 5 K when the field direction is applied and then reversed



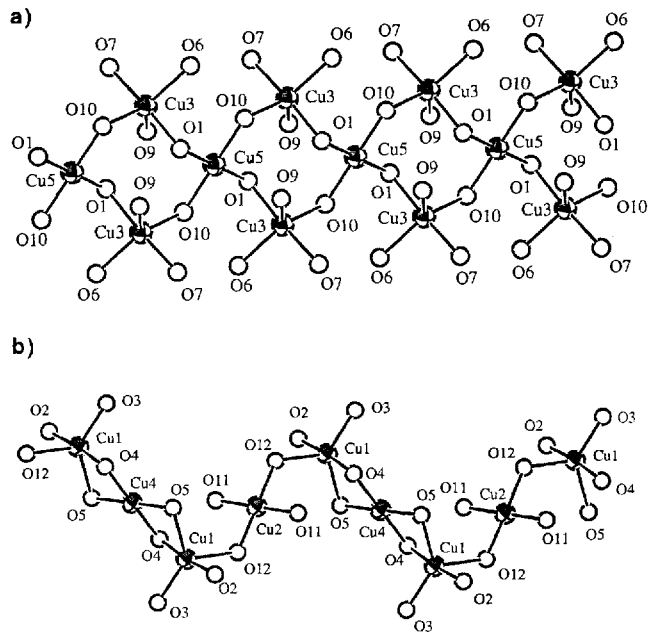
metry); the other two lie on general positions. The copper ions on the special positions, Cu(2), Cu(4) and Cu(5), possess a square planar coordination arrangement from four oxygen atoms derived from the AsO_4 groups. The other two copper ions, Cu(1) and Cu(3), possess slightly distorted trigonal bipyramidal arrangements with five nearest neighbor oxygen atoms derived from the AsO_4 groups. The square planar copper ions are linked into chains by the sharing of oxygen atoms with the trigonal bipyramidal copper ions. A structural diagram of **2** showing the two independent chains is shown in Figure 5. The chain composed of the copper atoms Cu(3) and Cu(5) (Figure 5a) contains eight-membered CuO rings in its repeating unit. Cu(5) has a square planar geometry. The other chains are composed of the copper atoms Cu(1), Cu(2) and Cu(4) (Figure 5b). Cu(2) and Cu(4) have square planar geometries. Both are linked by the trigonal bipyramidally pentacoordinated copper ions. A pair of *cis*-oxygen atoms on Cu(4) are coordinated to Cu(1) by using one of the axial and one of the equatorial coordination sites. A pair of *trans*-oxygen atoms on Cu(2) are linked to two Cu(1) atoms in an equatorial site. The compound $BaCu_2(AsO_4)_2$ was recently reported and shown to contain trigonal bipyramidally pentacoordinated copper ions also[13].

Table 2. Selected interatomic distances with esds for $Ba_2Cu_7As_6O_{24}$ (**2**)

Ba(1)–Cu(2)	3.7532(5)	Cu(1)–O(2)	1.905(6)
Ba(1)–Cu(3)	3.763(1)	Cu(1)–O(3)	1.985(5)
Ba(1)–O(2)	2.710(5)	Cu(1)–O(4)	1.996(6)
Ba(1)–O(3)	2.840(5)	Cu(1)–O(5)	2.135(5)
Ba(1)–O(7)	2.870(6)	Cu(1)–O(12)	2.229(5)
Ba(1)–O(8)	2.667(6)	Cu(2)–O(11)	1.900(5)
Ba(1)–O(8′)	2.599(6)	Cu(2)–O(11′)	1.900(5)
Ba(1)–O(9)	2.727(5)	Cu(2)–O(12)	1.975(5)
Ba(1)–O(11)	2.654(6)	Cu(2)–O(12′)	1.975(5)
Ba(1)–O(12)	3.018(5)	Cu(3)–O(1)	1.959(5)
As(1)–O(1)	1.717(5)	Cu(3)–O(6)	2.082(6)
As(1)–O(2)	1.698(5)	Cu(3)–O(7)	1.933(5)
As(1)–O(8)	1.662(5)	Cu(3)–O(9)	2.110(5)
As(1)–O(9)	1.687(6)	Cu(3)–O(10)	2.059(5)
As(2)–O(4)	1.697(5)	Cu(4)–O(4)	1.963(5)
As(2)–O(7)	1.662(6)	Cu(4)–O(4′)	1.963(5)
As(2)–O(11)	1.680(5)	Cu(4)–O(5)	1.985(5)
As(2)–O(12)	1.702(5)	Cu(4)–O(5′)	1.985(5)
As(3)–O(3)	1.687(5)	Cu(5)–O(1)	1.986(5)
As(3)–O(5)	1.692(5)	Cu(5)–O(1′)	1.986(5)
As(3)–O(6)	1.682(5)	Cu(5)–O(10)	1.955(6)
As(3)–O(10)	1.724(6)	Cu(5)–O(10′)	1.955(6)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

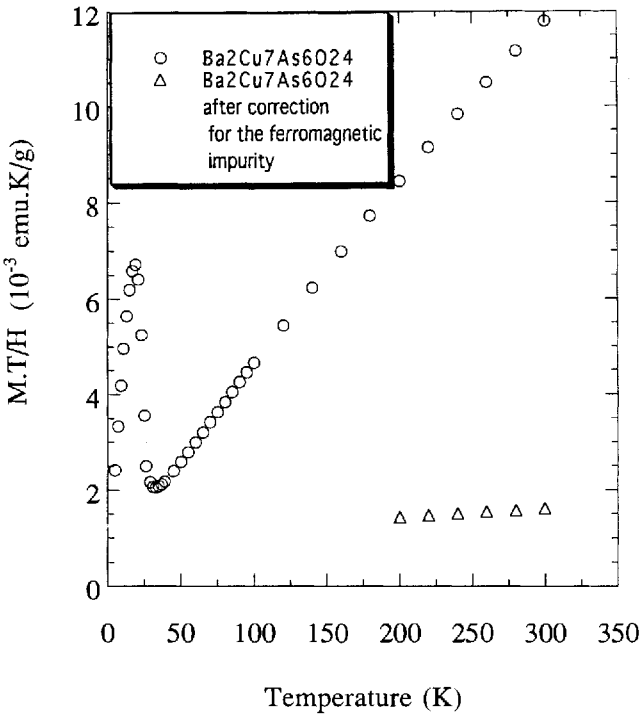
Figure 5. Structural diagrams showing the two independent chains of CuO groupings in the lattice of $Ba_2Cu_7As_6O_{24}$ (**2**): (a) chain formed by Cu(3) and Cu(5); (b) chain formed by Cu(1), Cu(2) and Cu(4)



Plots of MT/H versus temperature for **2** are shown in Figure 6. An initial ZFC measurement at H = 5 kOe revealed a strong increase of the magnetic moment below 30 K, as observed for **1**, but the MT/H ratio in the temperature range up to 200–300 K was found to be field dependent. This is attributed to the presence of a ferromagnetic (or ferrimagnetic) impurity with $T_c > 300$ K. Correction for this impurity was made by using the method of Honda and Owen[14]. To do this, isothermal magnetization scans were

recorded up to 45 kOe at 20 K intervals between 200 and 300 K. All curves showed first a saturation followed by a linear regime $M = M_o + \chi H$, where M_o is attributed to the saturated moment of the ferromagnetic impurity and χ is the paramagnetic susceptibility of **2**. This analysis gave a constant $M_o = 0.175(1)$ emu per gram of sample, which corresponds to about $N = 0.00003$ mol of hypothetical S = 1/2 spins per gram of sample (assuming $M_o = NgS\mu_B$). The ferromagnetic response in these samples in the region below 30 K may be due to **2** or the impurity, although it seems unlikely that the impurity is **1** since the response in **2** is stronger than that in **1**. Assuming that the mass of the impurity is negligible, we can calulate a magnetic moment of $\mu = 1.9$ B.M./Cu atom at 300 K after correction by using the formula $\mu_{eff}/\mu_B = (8\chi T)^{1/2}$ (where χ is expressed in emu/Cu mol). This is an acceptable value for Cu(II) with one unpaired electron. Ferrimagnetism has been observed for the compound $Ca_3Cu_3(PO_4)_4$ in the solid state[15]. This compound has been show to possess 1D chains of square planar Cu(II) ions linked by the $[PO_4]^{3-}$ groups. A similar effect may be responsible for the ferromagnetic response observed for **2**.

Figure 6. A plot of *MT/H* versus temperature (K) of a sample of **2**. (○) before correction for a trace of ferromagnetic impurity; (△) after correction



Experimental

The reagents $BaCO_3$ (99.98%), CuO (99.9%) and $As_2O_5 \cdot xH_2O$ (99.99%) were purchased from Aldrich. These were used without further purification. The reaction mixtures were heated in a Thermolyne Model F46120CM oven in an atmosphere of air. X-ray diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated MoK_α radiation. Scanning electron microscopy measurements were performed on a Hitachi S-2500Λ scanning electron microscope using a Kevex energy dispersion analyser at the University of South Carolina Electron Microscopy laboratory.

Synthesis of $Cu_4(AsO_4)_2O$ (**1**) *and $Ba_2Cu_7As_6O_{24}$* (**2**): A mixture of 0.4748 g (2.406 mmol) of $BaCO_3$, 0.6690 g (8.409 mmol) of CuO, and 0.9570 g (3.600 mmol) of $As_2O_5 \cdot xH_2O$ was ground thoroughly in a mortar, and then transferred to a ceramic crucible. The crucible was then placed in the oven and heated in air to 1090°C for 72 h. After the heating period, the oven was cooled slowly (approx. 5°C/min) to 600°C, then cooled rapidly to room temperature. Dark green crystals of $Cu_4(AsO_4)_2O$ (**1**) are readily distinguished and easily separated from the matrix mixture. The yield is estimated to be 20–30%. Analysis: relative metal % composition Cu/As % calc 63:37; % found: 63:37. It is notable that this green product was not obtained when appropriate quantities of CuO and $As_2O_5 \cdot xH_2O$ were heated to 1090°C in the *absence* of $BaCO_3$. Small quantities of a second product in the form of light gray to colorless crystals were also obtained from this reaction mixture. These have been identified as $Ba_2Cu_7As_6O_{24}$ (**2**). The yield of **2** appears to be considerably lower than that of **1**. Small amounts of monoclinic CuO were also found in the reaction mixtures[16]. Analysis: relative metal % composition Ba/Cu/As % calc 24:38:38; % found: 24:34:42.

Magnetic Measurements: Magnetic measurements were performed on a Quantum Design SQUID magnetometer using a polycrystalline sample. The susceptibility measurements on **1** were performed on a sample that was first cooled to 5 K in the absence 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 to be -176.10^{-6} emu/mol using the Pascal's constants). The mean room temperature magnetic moment, $\mu_{eff} = 1.95$ B.M./Cu, was calculated by using the formula $\mu_{eff}/\mu_B = (8\chi T)^{1/2}$ (where χ is expressed in emu/Cu mol). Hysteresis measurements were performed at 5 K by increasing the field (0–45000 Oe) and then decreasing it (40000–0 Oe).

Magnetic moments for a 51.2-mg polycrystalline sample of **2** were obtained in the temperature range 5–300 K. All data were corrected for the effect of the sample holder. Isothermal magnetization measurements showed that the *M/H* ratio was not field independent at temperatures up to 300 K. The presence of a ferromagnetic (or ferrimagnetic) impurity with $T_c > 300$ K was thus suspected. Correction for this impurity was made by using the method of Honda and Owen[15]. For this, isothermal magnetization scans were recorded up to 45 kOe for several temperatures between 200 and 300 K. All curves showed first a saturation followed by a linear regime $M = M_o + \chi H$ where M_o is attributed to the saturated moment of the magnetic impurity and χ is the paramagnetic susceptibility of **2**. This analysis gave a constant $M_o = 0.175(1)$ emu per gram of sample, which corresponds to about $N = 3 \times 10^{-5}$ mol of hypothetical S = 1/2 spins per gram of sample (writing $M_o = NgS\mu_B$). Assuming that the mass of the impurity is negligible, the magnetic moment is calculated to be $\mu = 1.9$ B.M./Cu atom at 300 K.

Crystallographic Analyses: Single crystals of **1** and **2** suitable for X-ray diffraction analysis were cleaved from the bulk material in the crucibles in which the preparations were carried out. A dark green crystal of **1** and a gray/colorless crystal of **2** were cleaved from the bulk sample by using a scalpel. The crystals used for the intensity measurements were mounted in thin-walled glass capillaries. The unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection pa-

rameters, and results of the analyses are listed in Table 3. All data processing was performed on a Silicon Graphics INDIGO2 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz-polarization (Lp) correction and an empirical absorption correction (based on three azimuthal psi scans) were applied in both of the analyses. Neutral atom scattering factors and anomalous dispersion corrections were applied to all atoms[17]. Full matrix least-squares refinements minimized the function: $\Sigma_{hkl}w(|F_o|-|F_c|)^2$ where $w = 1/\sigma(F1)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Table 3. Crystallographic data for compounds **1** and **2**

Compound	**1**	**2**
Formula	$Cu_4As_2O_9$	$Ba_2Cu_7As_6O_{24}$
Formula weight	548.02	1553.00
a (Å)	8.253(1)	8.4200(8)
b (Å)	6.4122(8)	11.420(2)
c (Å)	13.789(3)	5.2097(8)
α(°)	90.0	90.28(2)
β (°)	90.0	93.60(2)
γ(°)	90.0	89.12(2)
V (Å^3)	729.7(2)	499.9(1)
Space group	*Pnma* (#62)	*P*1bar (#2)
Z	4	1
Temperature (°C)	20	20
1 $K\alpha$(Mo)	0.71069 Å	0.71069 Å
ρ_{calc} (g/cm^3)	4.99	5.16
μ (Mo $K\alpha$) (cm^{-1})	205.34	211.38
No. obs. [$I > 3\sigma(I)$]	1505	2221
Goodness of fit (GOF)[a]	3.12	3.11
R[a]	0.038	0.040
R_w[a]	0.043	0.050

[a] $R = \Sigma_{hkl}(||F_{obs}|-|F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|^2)/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF = $[\Sigma_{hkl}(w(|F_{obs}|-|F_{calc}|)^2)/(n_{data} - n_{vari})]^{1/2}$.

For **1** the patterns of systematic absence observed in the data were consistent with either of the space groups *Pnma* or *Pna2*$_1$. The centrosymmetric space group *Pnma* was selected as the starting point and was confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters.

Compound **2** crystallized in the triclinic crystal system. The space group *P*1bar was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters[18].

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[18] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59337.

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