BaCu$_5$Al$_8$: A Structure Containing Interconnected [Al$_8$Cu$_4$]$^{2-}$ Icosahedra

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BaCu$_5$Al$_8$ was synthesized from stoichiometric amounts of the elements by heating in a tube furnace or melting in an arc welder. BaCu$_5$Al$_8$ forms a variation of the NaZn$_{13}$ structure in which large Ba^{2+} cations are surrounded by a three-dimensional network of interconnected Cu-centered, [Al$_8$Cu$_4$]$^{2-}$ icosahedra. The compound was characterized by both powder and single crystal X-ray diffraction. BaCu$_5$Al$_8$ crystallizes in the space group $Fm\bar{3}c$ (no.226); a = 12.2049(38) Å; Z = 8; R = 0.018; Goof = 1.16. EuCu$_5$Al$_8$ was characterized by powder X-ray diffraction, and lattice parameters were refined from the measured 2-theta values; a = 11.9715(19) Å. Magnetic susceptibility for both BaCu$_5$Al$_8$ and EuCu$_5$Al$_8$, and resistivity measurements on EuCu$_5$Al$_8$ are reported. Extended Hückel calculations on stoichiometries ranging from BaCu$_{13}$ to BaCuAl$_{12}$, demonstrate the tuning of the system's stoichiometry to balance the Fermi energy and overlap populations.

INTRODUCTION

The cluster chemistry of the group 13 elements involves an unusually rich and diverse collection of both nonmetal and metal cluster compounds. Volumes have been written about the cluster chemistry of boron, and recent work has revealed new cluster structures involving the heavier group 13 members.[1] An analogous cluster chemistry involving aluminum, however, has not been as forthcoming as one might expect based solely on its position in the periodic table: directly under boron and above gallium, whose cluster chemistry is well documented. A few cases aside,[2] aluminum is not traditionally considered an element with a rich cluster chemistry. (RE)Cu$_6$Al$_6$, (RE = La, Ce, Pr, Nd, Sm, Eu)[3] are reported in the NaZn$_{13}$ structure based

on X-ray powder diffraction, but no detailed crystallography nor single crystal work have been published.

In order to explore aluminum's ability to form cluster compounds, we are investigating the ternary systems AE-Cu-Al and RE-Cu-Al, and report here a single crystal investigation of the new compound $BaCu_5Al_8$. The observation of $BaCu_5Al_8$ in the $NaZn_{13}$[4] structure with aluminum and copper in icosahedral positions is particularly interesting with respect to both cluster chemistry of aluminum and any homogeneity width in the $(RE)Cu_xAl_{13-x}$ system. These new ternary compounds represent a transition from aluminum in delocalized, three dimensional structures with metallic behavior, to localized, electron-precise structures with semiconducting behavior. These new compounds contain aluminum and copper in icosahedra, but they are not isolated clusters. This is, instead, a network of interconnected icosahedra forming large cavities in which the barium atoms reside as large counter-cations. Along with the synthetic chemistry pursued with these new ternary compounds, some extended Hückel calculations were used to investigate the bonding in these icosahedral cluster compounds.

EXPERIMENTAL

Synthesis

Intermetallic materials of varying shoichiometries were prepared by reacting the elements: Ba rod (Johnson-Matthey Electronics, 99.5% purity), Al foil, Cu powder (Johnson-Matthey, 99.5% purity), Eu and La large shot (Ames Lab Rare-Earth Metals Processing, 99.0% purity). These elements were loaded in Al_2O_3 crucibles and sealed in evacuated quartz ampoules in an Ar-filled glove box and heated in a tube furnace, or melted in an argon filled, water cooled arc welder with a titanium getter for further argon purification. Reactions in tube furnaces followed the heating program: 25 °C to 1100 °C ($\sim$ 5 °C/min), 1 hour soaking at 1100 °C, slowly cooling to 25 °C ($\sim$ 2 °C/min). For samples melted in the arc welder, reactants were surrounded by Al foil, melted, and, in some cases, remelted several times after turning the resulting buttons over. Products from both synthetic methods were generally silver-gray metallic in appearance, and were increasingly brittle with an increasing Al content. The $BaCu_5Al_8$ structure reported here was solved from a crystal fragment picked from a crucible/tube furnace reaction loaded with the stoichiometry $BaCu_2Al_9$. Reactions with a variety of Cu : Al ratios were carried out using both synthetic techniques. See Table I for a summary of our synthetic results.

In many of these cases, the $BaCu_5Al_8$ phase was identified in the powder pattern, sometimes as the only phase, and often mixed with other binaries. Since Ba is a large divalent metal cation in this structure, synthesis has been attempted with other large di- and trivalent metals as well, and single crystal work has begun on products from the MCu_5Al_8 (M = Sr, Eu, La) systems, with preliminary results indicating products with a similar stoichiometry and structure as $BaCu_5Al_8$.[5]

TABLE I

Synthesis with varying stoichiometries

Reaction stoichiometry	Heating method	Reaction products (by powder X-ray diffraction)
$BaCu_{13}$	arc welder	$BaCu_{13}$ (see Ref. 12)
$BaCu_6Al_7$	furnace and arc welder	$BaCu_5Al_8$
$BaCu_5Al_8$	furnace and arc welder	$BaCu_5Al_8$
$BaCu_4Al_9$	arc welder	$BaCu_5Al_8$
$BaCu_3Al_{10}$	furnace	$BaCu_5Al_8 + CuAl_2 + Al$
$BaCuAl_{12}$	furnace and arc welder	unknown
$BaAl_{13}$	arc welder	unknown

TABLE II

Structure determination summary for BaCu5Al8

Space group	$mF\overline{3}c$ (no. 226)
Unit cell dimensions	a = 12.205(4) Å
Volume	1815.8(10) Å^3
Z	8
Density (calc.)	4.946 g cm^{-3}
Crystal size/mm	0.50 × 0.30 × 0.20
Absorption coefficient	16.776 mm^{-1}
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature/K	298(1)
2Θ range	2.0 to 60.0°
Scan range (ω)	0.60°
Scan speed	variable, 1.0 to 10.0 °/min in ω
Index ranges	$0 \leq h \leq 12$, $-16 \leq k \leq 16$, $-16 \leq l \leq -16$
Reflections collected	8415
Independent reflections	117 (R_{int} = 0.0843)
Observed reflections	115 ($F_o \geq 4.0\ \sigma\ (F_o)$)
Min./max. transmission	0.3495 / 0.9006
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0015F^2$
Parameters refined	13
R indices [$F_o \geq 4\sigma\ (F_o)$]	R = 0.0186, wR = 0.0452
R indices (all data)	R = 0.0188, wR = 0.0452
Goof* (all data)	1.16
Data-to-parameter ratio	8.4 : 1
Largest difference peak	+0.87 e/Å^{-3}
Largest difference hole	−1.24 e/Å^{-3}

* Goof = Goodness of fit

Structure Determination

Analysis of reaction products was carried out by both the powder X-ray analysis using an Enraf-Nonius Guinier camera (Cu Kα1 with Si internal standard) and single crystal analysis of BaCu5Al8 on a Siemens (Mo Kα1) diffractometer. A silver, irregularly shaped crystal taken from the reaction products was loaded, under air, into a capillary and sealed. Using high angle reflections ($2\Theta > 30$ degress), a lattice parameter of 12.205(4) Å was refined with a fit of 6.73. Further relevant crystallographic data are summarized in Table II.

Using single crystal X-ray diffraction, a face-centered cubic unit cell with Laue symmetry $m\overline{3}$ was indexed from a group of 30 reflections in the 2Θ range from 15° to 30°. A data set of 117 unique reflections and absorption correction reflections was collected on a Siemens P4 diffractometer at 298 ± 1 K. Lorentz and polarization corrections were applied, and a nonlinear correction based on the decay in the standard reflections was applied to the data set. A series of azimuthal reflections was collected and a semi-empirical absorption correction based on these scans was applied. The structure was solved by direct methods while refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using the SHELXTL-PLUS[6] programs. Positional and displacement parameters are summarized in Table III. (A compilation of all the crystallographic data, both single crystal and powder X-ray diffraction measurements may be obtained upon request from the authors).

TABLE III

Positional coordinates and equivalent isotropic displacement coefficients for BaCu5Al8

Atom	Site	x	y	z	U_{eq}	Site occ.
Ba	8a	1/4	1/4	1/4	0.0065(3)	1.0
Cu1	8b	0	0	0	0.0147(5)	1.0
Al	96i	0.1166(1)	0.1755(1)	0	0.0138(4)	0.322(3)
Cu2	96i	0.1166(1)	0.1755(1)	0	0.0138(4)	0.178(3)

EuCu5Al8 was synthesized in the arc welder by reaction of the elements and analyzed by powder X-ray diffraction. Using high angle reflections ($2\Theta > 30$ degrees), a lattice parameter of $a = 11.972(2)$ Å was refined with a fit of 3.48. Single crystal work is in progress and preliminary results suggest an *fcc* unit cell with a lattice parameter smaller than BaCu5Al8, in agreement with the powder data.

Physical Measurements

Magnetic susceptibilities were measured on BaCu5Al8 and EuCu5Al8 samples, using a SQUID magnetometer. Measurements were made from 6 K to 300 K at a field strength of 3 Tesla (30 000 Gauss). After making a diamagnetic core correction,

the EuCu5Al8 material showed classical paramagnetic behavior with a large signal and an effective moment of 7.82(2) Bohr magnetons, for $T > 80$ K, corresponding to Eu^{2+}. Magnetic hysteresis measurements were made on the EuCu5Al8 sample, at 50 K, 75 K and 100 K. The BaCu5Al8 compound showed temperature independent paramagnetism above 100 K ($X_{TIP} = 1.0 \times 10^{-4}$ emu/mol), with a tail at low temperatures, possibly due to a paramagnetic impurity.

In previous work on ternary lanthanide aluminides (EuFe4Al8, EuMn4Al8, EuCu4Al8, EuFe6Al6, and EuCu6Al6, all forming the ThMn12 structure[7,3]) Eu is reported as divalent or mixed valent. The evidence for such an assignment comes mostly from the larger unit cell volumes of the Eu compounds compared with the traditionally trivalent rare-earth elements forming the same compounds.

To complement the magnetic data which supported an f^7 configuration on the Eu, X-ray Photoelectron Spectroscopy (XPS) was carried out on a PHI 5500 Multi-Technique Surface Analysis Equipment for samples of EuCu5Al8 and EuAl4 in order to get core binding energies for Eu. EuAl4 was selected as a potential standard for Eu^{2+} in an aluminide structure found for all the alkaline earth aluminides.[8] When analyzing for Eu metal (*i.e.* Eu^0) using XPS, two of the most intense peaks occur at 1125 and 1154 eV corresponding to the 3d shell. For both EuAl4 and EuCu5Al8, peaks for these same two Eu core binding energies ooccurred. The XPS data for freshly made EuAl4 suggested that it was inappropriate to consider it as a model for Eu^{2+}, based on the equivalence of binding energies for Eu in EuAl4 and those of Eu metal. We hypothesize that there is a mixing of the Eu valence 6s, 6p, and 5d orbitals with the [Cu5Al8] framework, which makes a formal oxidation state of Eu difficult to assign. We are continuing to investigate this issue.

Resistivity measurements were made on the EuCu5Al8 sample using the Q-method.[9] The sample was prepared by mixing 60 mg of EuCu5Al8 powder (< 150 μm particle size) with dry Al2O3 powder in a Pyrex tube, which was then evacuated and sealed. Measurements on the »Q« meter were made at temperature intervals from -174 °C to 0 °C, with the sample both in and out of the coil. The sample resistivity (ρ) was calculated from the data from the equation: $\rho = 4.84 \times 10^5 \times (Va^2)/\Delta(1/Q)$ (Ω m), where V is the volume of the sample (m^3), a is the radius of the particles (m), and $\Delta(1/Q) = 1/Q_{in} - 1/Q_{out}$. The resistivity of the EuCu5Al8 sample was 122(10) μΩ cm at 293 K and 99(7) μΩ cm at 100 K. The data between 100 K and 293 K was fitted to the equation $\rho = 87(5) + 0.12(2)T$. The resistivites of Cu and Al metal are 1.75 and 2.824 μΩ cm at 293 K, respectively.

Theoretical Calculations

The electronic structures of these compounds were evaluated using the LCAO approximation in extended Hückel calculations.[10] Barium atoms were treated as classical cations, donating two electrons to the metallic [Cu_xAl_{13-x}] framework, and, therefore, no specific orbital contributions from the barium atoms were considered. Density of states (DOS) and crystal orbital overlap population (COOP) curves were determined by summing over a special k-point set (60 k-points in the irreducible wedge of the first Brilloun zone). The parameters of the atomic orbitals[11] used in the calculations are given in Table IV.

TABLE IV

Atomic parameters for extended Hückel calculations

Element	Atomic orbital	H_{ii}/eV	ζ_1	C1	ζ_2	C2
Cu	4s	−11.40	2.20			
	4p	−6.06	2.20			
	3d*	−14.00	5.95	0.5933	2.30	0.5744
Al	3s	−12.30	1.37			
	3p	−6.50	1.36			

* Double ζ Slater-type orbitals used for the Cu 3d

DISCUSSION

Structural Description

The $BaCu_5Al_8$ structure is a variation of the $NaZn_{13}$ structure. The structure has a face-centered cubic unit cell, as shown in the packing diagram of Cu-centered icosahedra and Ba^{2+} cations, Figure 1a. In Figure 1b, a clearer section of the structure is shown with the icosahedra surface bonding highlighted.
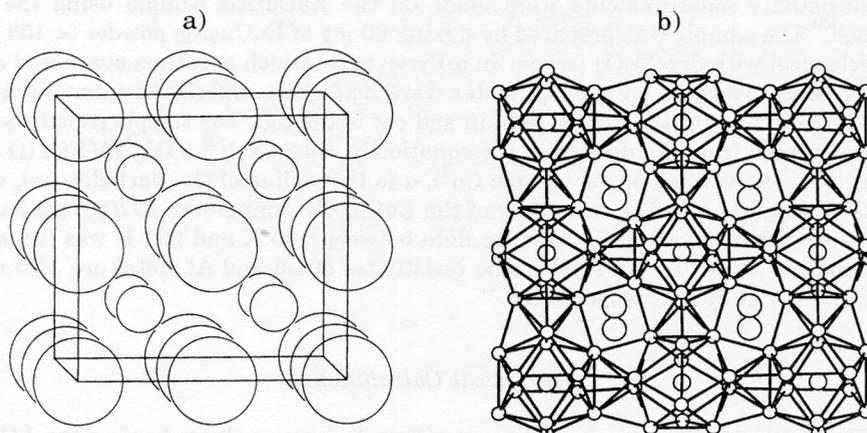
a)   b)

Figure 1. a) Unit cell »packing« of the Ba^{2+} cations and the large Cu-centered icosahedra. Icosahedra are large circles at (0, 0, 0), and the Ba^{2+} cations are the smaller circles at (0.25, 0.25, 0.25).
b) A section of the $BaCu_5Al_8$ complete structure is shown where the large circles are Ba atoms and the smaller circles make up the interconnected icosahedral network of Cu and Al atoms.

The data refined equally well in the noncentrosymmetric space group $F\bar{4}3c$ (no. 219), with Pearson's symbol $cF112$, with the icosahedra slightly tilted, thus destroying the mirror symmetry of the centrosymmetric $Fm\bar{3}c$ (no. 226). The structure can be built by starting with a Ba atom in the center of a cube and adding a Cu-centered icosahedron (Figure 2a) on each of the 8 corners of the cube. In the rather large unit cell of this structure, there are 8 such units, so the unit cell contents are $Ba_8Cu_8(Cu_{0.35}Al_{0.65})_{96}$. Based on the crystallographic data, the centers of the icosahedra are occupied by Cu(1) atoms (8a), and the icosahedral sites (96i) are randomly occupied by 4Cu(2) and 8Al atoms in $BaCu_5Al_8$. The surface (intra) icosahedral bonds are 2.630(5) Å, 2.694(5) Å, and 2.825(4) Å, and the inter-icosahedral bonds are 2.652(3) Å and 2.707(3) Å, while the bonds from the central Cu(1) atom to the icosahedral Cu(2) and Al atoms are slightly shorter at 2.562(2) Å. The Ba atoms are surrounded by a 24 vertex snub cube (Figure 2b), with distances from the Ba to the Cu(2) and Al atoms are 3.576(1) Å.
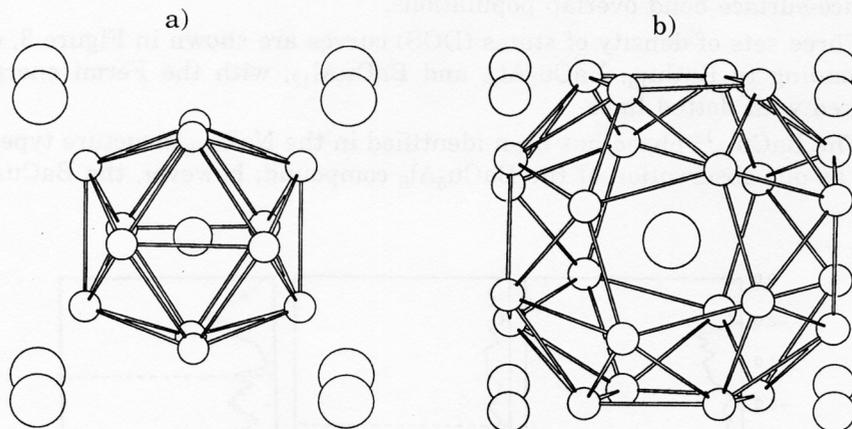
a)   b)

Figure 2. a) Cu-centered icosahedron (12 vertices). b) Ba-centered snub cube (24 vertices).

Theoretical Calculation Results

One question the calculations were designed to address was the following: is there an electronic or energetic reason why the ternary phase forms with the stoichiometry $BaCu_5Al_8$? Calculations aimed at providing some answers to this question proceeded by varying the Cu : Al ratio from $BaCu_{13}$, $BaCu_{12}Al...BaAl_{13}$ and considering the total density of states, Fermi ener-

Compound stoichiometry	Fermi energy/eV	COOP	
		Central-surface	Surface-surface (avg.)
$BaCu_{13}$	−10.62	0.0739	0.0713
$BaCu_8Al_5$	−8.06	0.1239	0.1713
$BaCu_6Al_7$	−7.33	0.1330	0.1708
$BaCu_5Al_8$	−7.03	0.1373	0.1679
$BaCu_4Al_9$	−6.45	0.1333	0.1626
$BaCuAl_{12}$	−4.65	0.1159	0.2323
$BaAl_{13}$	−4.35	0.1673	0.2215

gies, and COOP curves for the bonding in the icosahedra. Some of the results are summarized in Table V, including both central atom-surface and surface-surface bond overlap populations.

Three sets of density of states (DOS) curves are shown in Figure 3, corresponding to $BaCu_{13}$, $BaCu_5Al_8$, and $BaCuAl_{12}$, with the Fermi energies marked with dotted lines.

The $BaCu_{13}$[12] phase has been identified in the $NaZn_{13}$ structure type, as well as our observation of the $BaCu_5Al_8$ compound; however, the $BaCuAl_{12}$
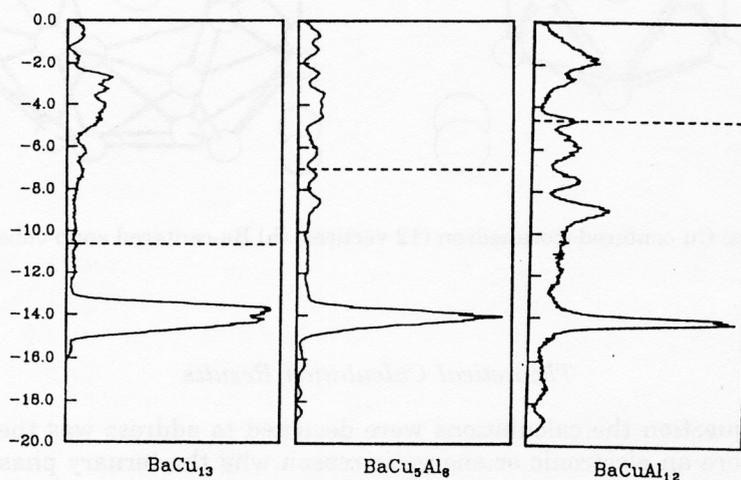

Figure 3. Total DOS curves for $BaCu_{13}$, $BaCu_5Al_8$, and »$BaCuAl_{12}$« from left to right as labeled. The Fermi energies (E_F/V) for each model are marked with a dotted line.

is merely a hypothetical composition in the $BaCu_5Al_8$ structure for these calculations. The DOS curves for all three are dominated by a strong and narrow Cu d-band between −15.0 and −13.0 eV, which broadens as the Cu concentration increases and, above which the DOS is dispersed and nearly featureless in the $BaCu_{13}$ and $BaCu_5Al_8$ curves. The features (i.e. peaks) in the $BaCuAl_{12}$ DOS curve between −9.0 and −4.0 eV correspond to high concentrations of molecular orbitals in the MO diagram of a single Al_{12} icosahedron taken from the structure. These features are smeared out as the Cu : Al ratio is increased and the bands are dispersed.

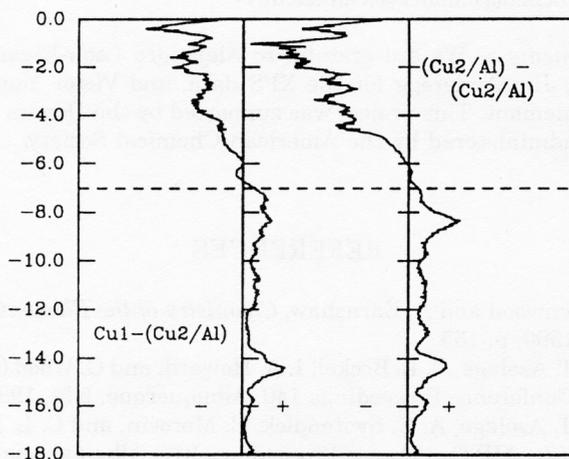Figure 4 contains the COOP curves for the icosahedral central atom-surface, and surface-surface bonds in $BaCu_5Al_8$.

Figure 4. COOP curves for the central atom-surface (Cu1 − Cu2/Al) and surface-surface bonding (Cu2/Al − Cu2/Al) in BaCu5Al8 are presented. The Fermi energy (−7.026 eV) is marked with a dotted line.

The COOP curves demonstrate an ideal situation which maximizes the bonding in $BaCu_5Al_8$, i.e. the Fermi energy crosses at the change from the bonding to anti-bonding character. In the Cu rich case ($BaCu_{13}$), with a low Fermi energy, there are many bonding states which are not filled, while in the Al rich case ($BaCuAl_{12}$), with a high Fermi energy, there are many antibonding states filled. The strength of the bonding, (i.e. overlap populations) between atoms forming the icosahedra varies as follows; Al-Al > Al-Cu > Cu-Cu. Interestingly, this trend does not change as the Cu : Al ratio changes. The Cu-Al and Cu-Cu bonding overlap populations are nearly equal for all the stoichiometries, but the strength of the Al-Al bonding increases as the Cu content increases.

Summary

We report the synthesis and X-ray structural characterization of the new compound $BaCu_5Al_8$, whose structure contains interconnected $[Al_8Cu_4]^{2-}$ icosahedra. Magnetic measurements on $BaCu_5Al_8$ and isostructural $EuCu_5Al_8$ are reported, as well as resistivity measurements for $EuCu_5Al_8$. Further characterization and physical property measurements are being pursued for many other alkaline earth, rare earth, and transition metal ternary aluminides.

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-825. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcrys.cam.ac.uk).

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SAŽETAK

BaCu5Al8: Struktura koja sadrži međusobno vezane ikozaedre [Al8Cu4]$^{2-}$

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Grijanjem u cijevnoj peći ili metodom lučnog taljenja stehiometrijskih količina elemenata priređen je BaCu5Al8. Spoj ima strukturu tipa NaZn$_{13}$ u kojoj su veliki kationi Ba^{2+} okruženi trodimenzijskom mrežom Cu-centriranih ikozaedara [Al8Cu4]$^{2-}$. Spoj je karakteriziran difrakcijom rentgenskih zraka na prahu i na monokristalu. BaCu5Al8 kristalizira u prostornoj grupi $Fm\overline{3}c$ (br. 226); a = 12.2049(38) Å; Z = 8; R = 0.018; Goof = 1.16. EuCu5Al8 je karakteriziran difrakcijom rentgenskih zraka na prahu, parametri jedinične ćelije određeni su iz vrijednosti 2-theta; a = 11.9715(19) Å. Dane su vrijednosti magnetskih susceptibilnosti za BaCu5Al8 i EuCu5Al8 kao i mjerenja električke otpornosti za EuCu5Al8. Računi proširenom Hückel-ovom metodom za stehiometrije od BaCu$_{13}$ do BaCuAl$_{12}$ pokazuju prilagodbu stehiometrije sustava Fermijevoj energiji i populaciji prekrivanja.