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$Eu_{14}MnSb_{11}$, a novel rare earth metal Zintl compound

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Abstract

A new rare earth metal Zintl compound, $Eu_{14}MnSb_{11}$, has been prepared in high yield from reacting stoichiometric amounts of the elements in a sealed tantalum tube, sealed in a quartz ampoule, at 1250 °C for 24 h. $Eu_{14}MnSb_{11}$ is isostructural with the Zintl compounds $A_{14}MPn_{11}$ (A = Ca, Sr, Ba; M = Al, Ga, Mn; Pn = As, Sb, Bi). Single crystal X-ray diffraction shows that this compound crystallizes in the tetragonal space group $I4_1/acd$, $a = 17.300(3)$ Å, $c = 22.746(4)$ Å, $T = 130$ K, $Z = 8$.

1. Introduction

There are a number of bonding schemes that account for the large variety of structures that have been discovered. One of these schemes is the Zintl concept [1–4] which can be used for a large number of solid state compounds. It employs relatively simple electron counting rules and was used first for binary materials composed of an alkali or alkaline earth metal and a main group element. In such compounds, the electropositive metal transfers its electrons to the electronegative element that can now form the correct number of homoatomic bonds so that finally each element has a complete octet.[5] Later, the Zintl concept was expanded to ternary materials and also referred to as the Zintl–Klemm[4,6] or the Zintl–Klemm–Busmann concept [1].

We have synthesized a series of transition metal compounds of the formula $A_{14}MnPn_{11}$ [7–11] that are isostructural to the main group Zintl compound, $Ca_{14}AlSb_{11}$ [12]. These compounds show a number of interesting properties. The Mn atoms are approximately 10 Å apart in all these compounds and are not connected through covalent bonding. Since a number of compounds with this structure type are ferromagnets with ordering temperatures as high as 65 K [9–11,13,14], we have been exploring the effect of cations and anions on this structure type [15]. In order to further explore the versatility of this structure type, we have synthesized a new compound $Eu_{14}MnSb_{11}$. This paper presents the synthesis and structure of this compound.

2. Experimental details

2.1. Synthesis

Eu metal was obtained from the Ames Laboratory and cut into small pieces; Mn flakes (99.9999%, J. Matthey) were cleaned with 10% HNO_3/CH_3OH solution, transferred to a dry box and ground into a powder; Sb shot (99.9999% J. Matthey) was also ground prior to use. The reactants and products were handled in nitrogen-filled dry boxes with typical water levels less than 1 ppm. Stoichiometric amounts of the elements were weighed in an Ar-filled dry box and put into a tantalum tube and sealed in an argon arc welder. The sealed tantalum tube was then sealed in a fused quartz tube under 60 Torr of purified Ar. Quantitative yield, as determined by Guinier X-ray powder diffraction, was obtained by heating the mixture up to 1250 °C for 24 h.

2.2. Single crystal X-ray diffraction

The tube was opened in a dry box equipped with a microscope and metallic looking needle shaped single crystals were separated and transferred to paratone N oil for X-ray structure determination. A suitable crystal was mounted on a glass fiber and positioned in a cold stream of nitrogen. The single crystal diffraction data were collected at 130 K on a Syntex $P2_1$ diffractometer equipped with a modified Lt-1 low temperature apparatus. Data collection parameters and crystallographic data are given in Table 1. The tetragonal I lattice was verified from axial photographs and systematic extinctions. No decomposition of the crystal was observed (inferred from the intensity of three check reflections). The data were corrected for Lorentz and polarization effects. Crystallographic programs used were those of shelxtl plus Version 4.0 [16]. Scattering factors and corrections for anomalous dispersion were from the *International Tables* [17]. The structure was refined by standard least squares methods with the initial positions

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TABLE 1. Data collection parameters and crystallographic data

Space group	$I4_1/acd$
Z	8
T	130 K
Lattice parameters (Å)	$a=17.300(3)$ $c=22.746(4)$
Cell volume (Å^3)	$V=6808(3)$
θ range	$0°<2\theta<55°$
Transmission coefficient range	0.0707–0.5025
Scan range (omega) (°)	1.00
Scan speed (min^{-1})	3.97
Number of collected reflections	3814
Number of unique reflections	1955
Number of observed reflections	1317 ($F>6.0\sigma(F)$)
Number of parameters refined	61
d_{calc} (mg m^{-3})	6.872
μ Mo Kα (mm^{-1})	34.249
R^a (%)	5.14
$R_w{}^b$ (%)	5.78

$^aR=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bR_w=\Sigma||F_o|-|F_c||w^{1/2}/\Sigma|F_ow^{1/2}|$.

TABLE 2. Atomic coordinates ($\Sigma10^4$) and equivalent isotropic displacement coefficients (Å$^2\times10^3$)

	x	y	z	U_{eq}
Sb(1)	1332(1)	3832(1)	1250	13(1)
Sb(2)	34(1)	1114(1)	8124(1)	14(1)
Sb(3)	8685(1)	9744(1)	9533(1)	14(1)
Sb(4)	0	2500	1250	16(1)
Mn	0	2500	8750	7(1)
Eu(1)	−435(1)	−732(1)	8278(1)	13(1)
Eu(2)	−214(1)	1241(1)	10(1)	15(1)
Eu(3)	3568(1)	0	2500	13(1)
Eu(4)	1808(1)	4089(1)	8429(1)	14(1)

TABLE 3. Anisotropic displacement coefficients (Å$^2\times10^3$)^a

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	12(1)	12(1)	14(1)	0(1)	0(1)	0(1)
Sb(2)	15(1)	13(1)	14(1)	−1(1)	1(1)	0(1)
Sb(3)	15(1)	13(1)	12(1)	3(1)	1(1)	0(1)
Sb(4)	16(1)	16(1)	17(2)	5(1)	0	0
Mn	9(2)	9(2)	4(3)	0	0	0
Eu(1)	13(1)	13(1)	15(1)	−1(1)	1(1)	0(1)
Eu(2)	13(1)	14(1)	17(1)	0(1)	0(1)	0(1)
Eu(3)	13(1)	13(1)	12(1)	0	0	2(1)
Eu(4)	13(1)	18(1)	13(1)	1(1)	−1(1)	−1(1)

^{a}The anisotropic displacement factor exponent takes the form $-2\pi^2(h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12})$.

taken from $Ca_{14}AlSb_{11}$ [12]. An absorption correction was applied [18] and the structure refinement proceeded without any problems. Atomic coordinates and displacement coefficients are given in Tables 2 and 3.

3. Structural results and discussion

The rare earth metal compound $Eu_{14}MnSb_{11}$ is isostructural with the main group Zintl metal compounds $A_{14}AlSb_{11}$ (A = Ca, Sr, Ba) [12,19] and $A_{14}GaAs_{11}$ (A = Ca, Sr) [20,21] and also the transition metal Zintl compounds $A_{14}MnPn_{11}$ (A = Ca, Sr, Ba; Pn = As, Sb, Bi) [11,15]. The $A_{14}MPn_{11}$ (M = Al, Ga) structure type can be described in the framework of the Zintl–Klemm concept consisting of $14A^{2+}$, $4Pn^{3-}$, MPn_4^{9-} and Pn_3^{7-} [12,20–22]. In the case of $Eu_{14}MnSb_{11}$, there are rare earth metal atoms, isolated Sb atoms, distorted $MnSb_4$ tetrahedra and linear Sb_3 chains. Figure 1 shows a perspective view of the unit cell. The $MnSb_4$ tetrahedra and the Sb_3 chains alternate with respect to one another along the *c*-axis. The chains are rotated by 90° with respect to one another along the *c*-axis. The chains and tetrahedra alternate with each other along the *a*- and *b*-axes as well, but are translated by a full unit cell dimension along these directions. Selected bond distances and angles can be found in Table 4.

The $MnSb_4$ tetrahedra are slightly distorted and flattened along the *a*–*b* plane. The angles are 118.6° and 105.1°. The main group analogs also have slightly distorted tetrahedra, for example, in $Ca_{14}AlSb_{11}$, the angles are 114.0° and 107.3° [12]. The increased distortion observed in the Mn compound compared with the main group analogs is attributed to the Jahn–Teller effect (Mn^{III} is a d^4 ion) [7], although steric effects probably also contribute [11,19].

The effect of the cation as a function of bond distances has been observed for all other compounds of this

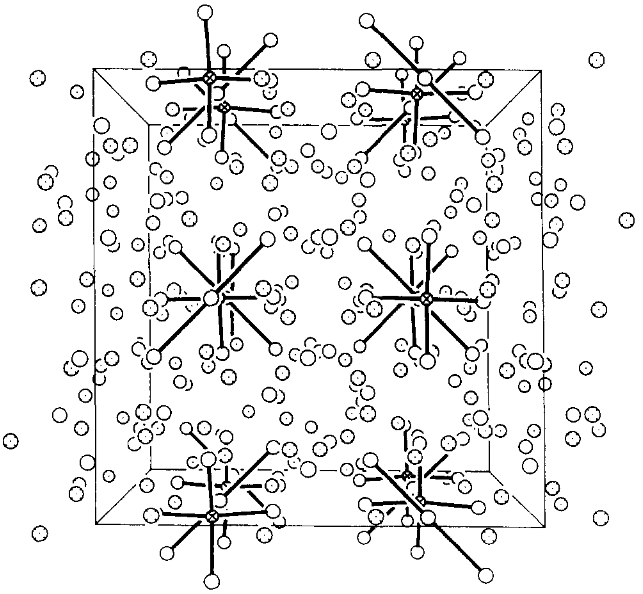

Fig. 1. A perspective view down the *c*-axis showing the unit cell for $Eu_{14}MnSb_{11}$. The Eu, Mn and Sb atoms are indicated by dotted, cross-hatched and open circles, respectively.

TABLE 4. Selected bond length (Å) and angles (°)

Sb(1)–Sb(4) 2x	3.258(2)	Sb(1)–Eu(1) 2x	3.326(2)
Sb(1)–Eu(2) 2x	3.421(2)	Sb(1)–Eu(3) 2x	3.493(1)
Sb(1)–Eu(4) 2x	3.329(2)		
Sb(2)–Eu(1′)	3.355(2)	Sb(2)–Eu(1)	3.313(2)
Sb(2)–Eu(2′)	3.267(2)	Sb(2)–Eu(2)	3.840(2)
Sb(2)–Eu(4)	3.282(2)	Sb(2)–Eu(3)	3.402(2)
		Sb(2)–Eu(4′)	3.522(2)
Sb(3)–Eu(1)	3.340(2)	Sb(3)–Eu(1′)	3.304(2)
Sb(3)–Eu(2)	3.393(2)	Sb(3)–Eu(2′)	3.313(2)
Sb(3)–Eu(3)	3.252(2)	Sb(3)–Eu(4)	3.333(2)
Sb(3)–Eu(4′)	3.298(2)	Sb(3)–Eu(4″)	3.851(2)
Sb(4)–Eu(1) 4x	3.329(1)	Sb(4)–Eu(2) 4x	3.581(1)
Mn–Sb(2) 4x	2.790(2)	Mn–Eu(2) 4x	3.619(1)
Mn···Mn	10.352(3)		
Sb(2)–Mn–Sb(2′)	118.6(1)	Sb(2)–Mn–Sb(2″)	105.1(1)

structure type published to date [11,15,19,21]. Bond distances increase with the size of the cation. The ionic radius of Eu^{2+} is between Ca^{2+} and Sr^{2+} and one would predict that the bond distances should fall somewhere in between those for the Ca and Sr analogs. The Mn–Sb distance of 2.790(2) Å is intermediate between the Ca and Sr analogs and within the range of distances observed for the $A_{14}MnSb_{11}$ (A = Ca, Sr, Ba) compounds (2.759 (2)–2.872 (3) Å) [15]. The Sb–Sb distance in the linear chain is 3.258(2) Å, slightly longer than that observed in the Ca analog (3.215(2) Å) and slightly shorter than that observed in the Sr analog (3.310(2) Å). The Sb–Sb distance is similar to those observed in the main group analogs, for example $A_{14}AlSb_{11}$ (3.196–3.370 Å). Typical bond lengths observed for Sb–Sb single bonds in solid state compounds are 2.84 Å in the Zintl compound, $Ca_{11}InSb_9$ [23], to 2.908 Å in elemental Sb [24]. The increased distance is consistent with the interpretation of a 2-center 4-electron bond [24].

The Sb^{3-} anions are located between the tetrahedra and the Sb_3^{7-} units and form a spiral along *c*. These anions are not considered to be part of a covalent unit. The shortest distances to other Sb are those within the spiral, 4.228 Å and 4.619 Å. They are coordinated by seven Eu cations with six short and one longer Eu–Sb distances.

Magnetic and transport properties of this compound are in progress.

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