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Crystal structure of tetrasodium octaeuropium(II) pentaphosphido(3–)-diphosphido(4–)-digallate(III) *catena*-triphosphido(3–)-diphosphido(4–)-digallate(III), $Na_4Eu_8[Ga_2P_5(P_2)][Ga_2P_3(P_2)]$

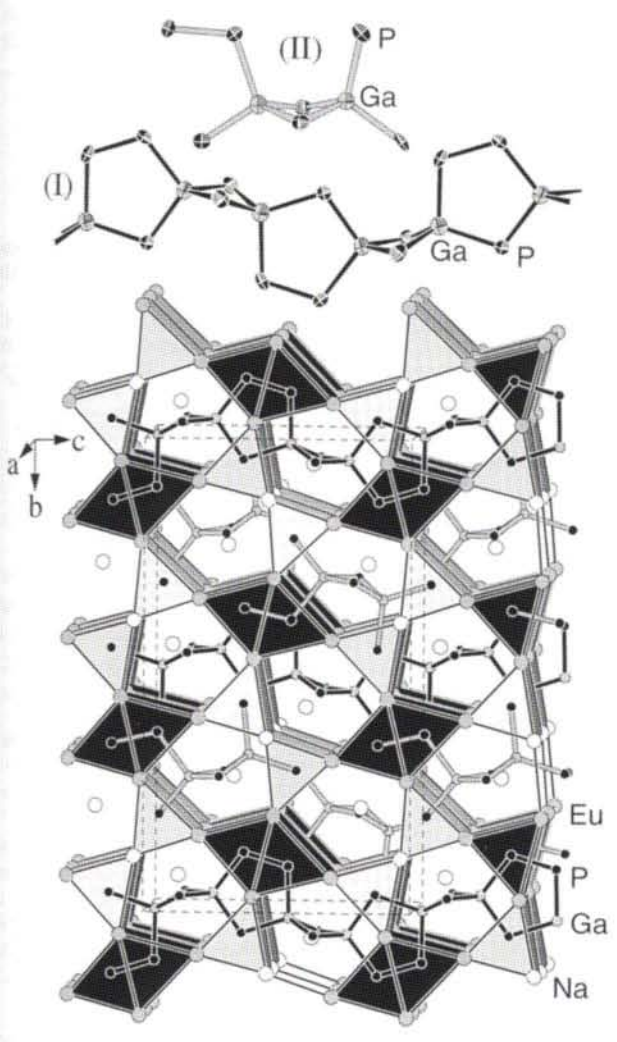
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Source of material: $Na_4Eu_8Ga_4P_{12}$ was prepared from the stoichiometric mixture of Na, EuP and GaP (ratio 1 : 2 : 1) in a sealed niobium ampoule at 1323 K.

The structure contains two novel types of metallate anions, namely infinite spiro-cyclic chains *catena*-$[Ga_2P_3(P_2)]^{7-}$ (I) and isolated $[Ga_2P_5(P_2)]^{13-}$ (II) with endocyclic $(P_2)^e$ and terminal $(P_2)^t$ dumbbells in (I) and (II), respectively. Mean bond lengths in (I): d(Ga–P) = 2.44 Å and d(Ga–P) = 2.39 Å in the five-membered and four-membered rings, respectively, and $d(P–P)^e$ = 2.22 Å; in (II): d(Ga–P) = 2.42 Å in the Ga_2P_2 ring, $d(Ga–P)^t$ = 2.40 Å and $d(P–P)^t$ = 2.30 Å. The partial structure of the cations forms a framework of condensed trigonal prisms with pentagonal channels, closely related to that of $Na_4Sr_8Al_4P_{12}$ (see ref. 1) and $Mg_2Ru_5B_4$ (see ref. 2). The atoms of the endocyclic and terminal (P–P) ligands occupy the centers of rhombic prisms (pairs of black trigonal prisms with a common rectangular face). The cyclic Ga_2P_2 fragments are in the channels. A partial replacement of Na by Eu is observed in the octahedral Na1 position, according to $2Na^+ = \square + Eu^{2+}$.

$Eu_8Ga_4Na_4P_{12}$, orthorhombic, $Cmc2_1$ (No. 36), a =8.984(1) Å, b =22.843(3) Å, c =12.814(2) Å, V =2629.7 Å^3, Z =4, $R(F)$ =0.051, $R_w(F)$ =0.051.

Table 1. Parameters used for the X-ray data collection

Crystal:	black prism, size 0.13 x 0.10 x 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	240.7 cm^{-1}
Diffractometer:	Siemens P4
Scan mode:	ω
$T_{measurement}$:	293 K
$2\theta_{max}$:	55°
$N(hkl)_{unique}$:	1804
Criterion for F_o:	$F_o > 4\,\sigma(F_o)$
$N(param)_{refined}$:	149
Program:	SHELXTL-plus

Table 2. Final atomic coordinates and displacement parameters (in $Å^2$)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)[a]	8*b*	0.2944(6)	0.3770(3)	–0.0246(6)	0.027(3)	0.028(3)	0.032(4)	–0.004(2)	–0.004(3)	0.001(2)
Na(2)	4*a*	0	0.4347(5)	0.109(1)	0.006(4)	0.016(5)	0.030(6)	0	0	0.007(5)
Na(3)	4*a*	0	0.2244(8)	0.314(2)	0.034(8)	0.046(9)	0.09(2)	0	0	–0.00(1)
Eu(1)	8*b*	0.2324(1)	0.21189(5)	0[b]	0.0291(6)	0.0281(6)	0.0313(7)	0.0006(4)	–0.0021(7)	–0.0029(5)
Eu(2)	8*b*	0.2182(1)	0.45867(5)	0.4233(2)	0.0272(5)	0.0288(6)	0.0366(7)	–0.0011(4)	–0.0002(6)	0.0019(5)
Eu(3)	8*b*	0.2395(1)	0.58344(6)	0.2164(2)	0.0317(6)	0.0276(6)	0.0262(7)	0.0017(4)	0.0004(5)	0.0002(5)
Eu(4)	8*b*	0.2619(1)	0.33034(6)	0.2207(2)	0.0309(6)	0.0280(6)	0.0285(7)	0.0012(4)	–0.0000(6)	0.0004(6)
Ga(1)	4*a*	0	0.9569(2)	0.2664(4)	0.028(2)	0.028(2)	0.025(2)	0	0	0.001(1)
Ga(2)	4*a*	0	0.0089(2)	0.5511(4)	0.034(2)	0.033(2)	0.027(2)	0	0	–0.002(2)
Ga(3)	4*a*	0	0.2887(2)	0.6772(4)	0.026(2)	0.031(2)	0.024(2)	0	0	–0.002(1)
Ga(4)	4*a*	0	0.6645(2)	0.3983(3)	0.028(2)	0.027(2)	0.024(2)	0	0	0.000(1)
P(1)	4*a*	0	0.1008(4)	0.0475(7)	0.029(4)	0.031(4)	0.022(4)	0	0	–0.008(4)
P(2)	4*a*	0	0.1293(4)	0.8820(7)	0.027(3)	0.022(3)	0.022(4)	0	0	0.004(3)
P(3)	4*a*	0	0.0422(4)	0.3735(8)	0.032(4)	0.027(4)	0.024(4)	0	0	–0.000(4)
P(4)	8*b*	0.2908(7)	0.4586(3)	0.1527(6)	0.026(3)	0.034(3)	0.028(3)	0.000(2)	–0.006(3)	–0.003(2)
P(5)	4*a*	0	0.3803(4)	0.5554(7)	0.028(4)	0.027(4)	0.026(4)	0	0	0.002(4)
P(6)	4*a*	0	0.3565(4)	0.3811(7)	0.023(3)	0.029(4)	0.021(4)	0	0	0.002(3)
P(7)	4*a*	0	0.7914(4)	0.0645(8)	0.025(4)	0.027(4)	0.029(5)	0	0	–0.001(4)
P(8)	4*a*	0	0.3024(4)	0.0769(8)	0.034(4)	0.027(4)	0.028(5)	0	0	–0.010(4)
P(9)	4*a*	0	0.5581(4)	0.3784(9)	0.030(4)	0.027(4)	0.036(5)	0	0	0.007(4)
P(10)	8*b*	0.2951(7)	0.2058(2)	0.2970(6)	0.024(3)	0.025(3)	0.030(3)	–0.000(2)	–0.003(3)	–0.001(2)

a: Na(1) occupancy = 0.82(2) Na and 0.09 Eu + 0.09 □.
b: arbitrarily fixed for definition of the origin.

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