Supplementary Materials: The Crystal Chemistry of Rathite Based on New Electron-Microprobe Data and Single-Crystal Structure Refinements: The Role of Thallium

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Table S1a. Fractional atomic coordinates and displacement parameters (in Å²) for sample rath3.

Site	Atom	Sof	*x*/*a*	*y*/*b*	*z*/*c*	U_{ani}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	Pb,Tl	1	0.47592(4)	0.75349(5)	0.20480(2)	0.03124(9)	0.02637(16)	0.02683(17)	0.0400(2)	−0.00066(14)	0.00473(13)	0.00276(13)
Pb2	Pb,Tl	1	0.97818(5)	0.75073(7)	0.20288(2)	0.05211(15)	0.0331(2)	0.0583(3)	0.0595(3)	0.0244(2)	−0.00557(18)	−0.0197(2)
As1	As	1	0.29776(9)	0.84994(11)	0.34079(3)	0.01890(15)	0.0160(3)	0.0219(4)	0.0196(3)	−0.0015(3)	0.0054(3)	0.0004(3)
As2	As	1	0.25091(10)	0.33117(10)	0.14814(3)	0.02180(16)	0.0293(4)	0.0161(3)	0.0212(4)	−0.0037(3)	0.0078(3)	−0.0068(3)
Me3a	As	0.899(10)	0.68833(16)	0.65586(14)	0.04382(5)	0.0442(4)	0.0651(8)	0.0289(6)	0.0466(7)	−0.0131(4)	0.0308(6)	−0.0204(5)
Me3b	Sb	0.101(10)	0.68833(16)	0.65586(14)	0.04382(5)	0.0442(4)	0.0651(8)	0.0289(6)	0.0466(7)	−0.0131(4)	0.0308(6)	−0.0204(5)
As4	As	1	0.13942(9)	0.66712(11)	0.05989(3)	0.01909(15)	0.0163(3)	0.0237(4)	0.0175(3)	0.0024(3)	0.0039(3)	−0.0004(3)
Me5a	As	0.546(2)	0.4271(2)	0.0328(3)	0.05071(8)	0.0328(3)	0.0285(5)	0.0456(7)	0.0257(7)	−0.0008(6)	0.0087(6)	0.0015(5)
Me5b	Ag	0.454(2)	0.4149(2)	0.0160(2)	0.07579(7)	0.0328(3)	0.0285(5)	0.0456(7)	0.0257(7)	−0.0008(6)	0.0087(6)	0.0015(5)
Me6a	Pb	0.897(3)	0.90488(4)	0.08944(5)	0.07197(2)	0.02801(12)	0.02564(17)	0.02926(19)	0.03097(19)	0.00345(14)	0.01004(13)	0.00848(13)
Me6b	As	0.103(3)	0.90488(4)	0.08944(5)	0.07197(2)	0.02801(12)	0.02564(17)	0.02926(19)	0.03097(19)	0.00345(14)	0.01004(13)	0.00848(13)
S1	S	1	0.2591(2)	0.0020(2)	0.26401(8)	0.0212(4)	0.0204(8)	0.0159(8)	0.0275(9)	0.0040(7)	0.0053(7)	0.0009(6)
S2	S	1	0.2506(2)	0.4790(2)	0.22379(8)	0.0191(3)	0.0212(8)	0.0174(8)	0.0190(8)	−0.0042(6)	0.0049(6)	−0.0004(6)
S3	S	1	0.5050(2)	0.6783(2)	0.32447(8)	0.0187(3)	0.0163(7)	0.0149(8)	0.0254(9)	0.0012(7)	0.0050(6)	0.0010(6)
S4	S	1	0.9062(2)	0.1708(3)	0.18100(8)	0.0213(4)	0.0232(8)	0.0187(8)	0.0237(9)	−0.0013(7)	0.0084(7)	0.0001(7)
S5	S	1	0.6941(2)	0.8406(2)	0.11266(8)	0.0200(3)	0.0200(8)	0.0170(8)	0.0225(8)	−0.0009(7)	0.0026(6)	−0.0001(6)
S6	S	1	0.1708(2)	0.8801(2)	0.12007(8)	0.0222(4)	0.0228(8)	0.0147(8)	0.0277(9)	0.0017(7)	0.0015(7)	−0.0010(7)
S7	S	1	0.3681(2)	0.5180(2)	0.09864(8)	0.0197(3)	0.0161(7)	0.0190(8)	0.0251(9)	0.0004(7)	0.0068(6)	−0.0012(6)
S8	S	1	0.9583(3)	0.5096(3)	0.09359(10)	0.0276(4)	0.0239(9)	0.0158(9)	0.0460(13)	−0.0008(8)	0.0139(9)	−0.0034(7)
S9	S	1	0.5867(3)	0.2010(3)	0.01128(11)	0.0338(5)	0.0254(10)	0.0263(11)	0.0489(14)	0.0097(10)	0.0048(9)	−0.0008(8)
S10	S	1	0.1790(2)	0.1840(3)	0.00847(8)	0.0240(4)	0.0239(9)	0.0255(10)	0.0232(9)	−0.0007(7)	0.0062(7)	−0.0045(7)

Table S1b. Fractional atomic coordinates and displacement parameters (in Å²) for sample rath4.

Site	Atom	Sof	*x*/*a*	*y*/*b*	*z*/*c*	U_{ani}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	Pb,Tl	1	0.47582(5)	0.75377(6)	0.20495(2)	0.0350(2)	0.0289(3)	0.0349(3)	0.0409(3)	−0.0008(2)	0.0058(2)	0.0030(2)
Pb2	Pb,Tl	1	0.97835(6)	0.75062(7)	0.20306(3)	0.0546(2)	0.0355(3)	0.0630(4)	0.0609(4)	0.0221(3)	−0.0025(3)	−0.0190(3)
As1	As	1	0.29825(12)	0.85045(14)	0.34117(4)	0.0225(3)	0.0178(6)	0.0300(7)	0.0210(6)	−0.0015(5)	0.0070(5)	0.0004(5)
As2	As	1	0.24901(14)	0.33249(14)	0.14765(5)	0.0259(3)	0.0356(7)	0.0230(6)	0.0212(7)	−0.0037(5)	0.0108(5)	−0.0080(5)
Me3a	As	0.922(10)	0.68687(17)	0.65599(16)	0.04285(6)	0.0464(6)	0.0646(10)	0.0376(8)	0.0445(10)	−0.0104(6)	0.0297(7)	−0.0167(7)
Me3b	Sb	0.078(10)	0.68687(17)	0.65599(16)	0.04285(6)	0.0464(6)	0.0646(10)	0.0376(8)	0.0445(10)	−0.0104(6)	0.0297(7)	−0.0167(7)
As4	As	1	0.13898(13)	0.66813(14)	0.05958(4)	0.0224(3)	0.0199(6)	0.0300(6)	0.0181(6)	0.0014(5)	0.0054(5)	−0.0005(5)
Me5a	As	0.540(3)	0.4279(5)	0.0319(5)	0.05093(15)	0.0365(6)	0.0328(9)	0.0542(11)	0.0249(19)	0.0009(15)	0.0119(15)	0.0016(8)
Me5b	Ag	0.460(3)	0.4148(4)	0.0143(4)	0.07619(13)	0.0365(6)	0.0328(9)	0.0542(11)	0.0249(19)	0.0009(15)	0.0119(15)	0.0016(8)
Me6a	Pb	0.866(4)	0.90434(6)	0.08886(7)	0.07177(2)	0.0332(2)	0.0298(3)	0.0396(4)	0.0321(4)	0.0026(2)	0.0108(2)	0.0105(2)
Me6b	As	0.134(4)	0.90434(6)	0.08886(7)	0.07177(2)	0.0332(2)	0.0298(3)	0.0396(4)	0.0321(4)	0.0026(2)	0.0108(2)	0.0105(2)
S1	S	1	0.2592(3)	0.0011(3)	0.26397(11)	0.0240(6)	0.0237(15)	0.0210(15)	0.0279(17)	0.0016(13)	0.0061(13)	−0.0003(12)
S2	S	1	0.2505(3)	0.4798(3)	0.22378(11)	0.0234(6)	0.0251(15)	0.0271(15)	0.0183(15)	−0.0040(12)	0.0051(12)	−0.0005(12)
S3	S	1	0.5053(3)	0.6787(3)	0.32494(12)	0.0219(6)	0.0167(14)	0.0240(15)	0.0257(16)	0.0010(12)	0.0058(12)	0.0028(11)
S4	S	1	0.9059(3)	0.1710(3)	0.18045(11)	0.0245(7)	0.0239(15)	0.0265(15)	0.0245(16)	−0.0014(13)	0.0078(12)	0.0008(12)
S5	S	1	0.6940(3)	0.8400(4)	0.11245(11)	0.0241(7)	0.0232(15)	0.0265(15)	0.0221(16)	0.0013(12)	0.0026(12)	0.0014(12)
S6	S	1	0.1702(3)	0.8802(3)	0.12011(11)	0.0256(7)	0.0274(15)	0.0215(15)	0.0270(16)	−0.0003(12)	0.0028(13)	−0.0009(12)
S7	S	1	0.3672(3)	0.5192(4)	0.09844(11)	0.0236(6)	0.0212(14)	0.0277(16)	0.0234(16)	−0.0009(12)	0.0084(12)	−0.0010(12)
S8	S	1	0.9585(3)	0.5088(4)	0.09316(13)	0.0325(7)	0.0247(15)	0.0225(16)	0.054(2)	0.0010(14)	0.0154(15)	−0.0028(12)
S9	S	1	0.5868(4)	0.2014(4)	0.01198(14)	0.0364(8)	0.0299(17)	0.0338(18)	0.045(2)	0.0068(15)	0.0069(15)	−0.0038(14)
S10	S	1	0.1794(3)	0.1835(4)	0.00891(12)	0.0283(7)	0.0288(16)	0.0337(17)	0.0236(17)	0.0006(13)	0.0080(13)	−0.0032(13)

Table S1c. Fractional atomic coordinates and displacement parameters (in Å²) for sample rath5 (from Berlepsch et al. [2]).

Site	Atom	Sof	*x*/*a*	*y*/*b*	*z*/*c*	U_{ani}
Pb1	Pb,Tl	1	0.47494(5)	0.75704(5)	0.20558(2)	0.0404(2)
Pb2	Pb,Tl	1	0.98078(5)	0.74922(6)	0.20540(2)	0.0598(2)
As1	As	1	0.29987(10)	0.85369(12)	0.34169(4)	0.0274(3)
As2	As	1	0.24640(12)	0.33506(12)	0.14689(45)	0.0311(2)
Me3a	As	0.735(9)	0.6847(5)	0.6605(5)	0.0417(2)	0.0437(10)

Me3b	Sb	0.265(9)	0.6884(12)	0.6243(14)	0.0380(4)	0.066(3)
As4	As	1	0.13800(10)	0.67143(12)	0.05873(4)	0.0276(2)
Me5a	As	0.526(10)	0.4257(3)	0.0252(4)	0.0510(3)	0.0352(8)
Me5b	Ag	0.474(10)	0.4162(3)	0.0111(4)	0.0772(2)	0.0448(10)
Me6a	Pb	0.739(4)	0.90270(12)	0.08494(16)	0.07178(3)	0.0379(3)
Me6b	As	0.261(4)	0.8732(11)	0.0374(14)	0.0780(4)	0.075(4)
S1	S	1	0.2564(3)	0.9974(3)	0.26341(10)	0.0313(5)
S2	S	1	0.2476(3)	0.4798(3)	0.22331(9)	0.0274(5)
S3	S	1	0.5068(3)	0.6830(3)	0.32623(9)	0.0262(5)
S4	S	1	0.9017(3)	0.1712(3)	0.17828(10)	0.0321(5)
S5	S	1	0.6976(3)	0.8377(3)	0.11176(9)	0.0291(5)
S6	S	1	0.1656(3)	0.8802(3)	0.12022(10)	0.0320(5)
S7	S	1	0.3641(3)	0.5211(3)	0.09716(9)	0.0289(5)
S8	S	1	0.9572(3)	0.5086(3)	0.08998(12)	0.0404(6)
S9	S	1	0.5888(3)	0.1974(3)	0.01482(12)	0.0434(7)
S10	S	1	0.1794(3)	0.1800(3)	0.01016(10)	0.0321(5)

Table S1d. Fractional atomic coordinates and displacement parameters (in Å^2) for sample rath7.

Site	Atom	Sof	*x*/*a*	*y*/*b*	*z*/*c*	U_{ani}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	Pb,Tl	1	0.47431(5)	0.76109(5)	0.20613(2)	0.03837(11)	0.03211(18)	0.0397(2)	0.0429(2)	−0.00134(16)	0.00598(15)	0.00546(16)
Pb2	Pb,Tl	1	0.98215(5)	0.74988(6)	0.20759(2)	0.05762(15)	0.0349(2)	0.0515(3)	0.0814(4)	0.0191(2)	−0.0022(2)	−0.0155(2)
As1	As	1	0.30149(10)	0.85825(12)	0.34316(4)	0.02781(19)	0.0209(4)	0.0304(4)	0.0335(5)	−0.0041(4)	0.0084(3)	0.0026(3)
As2	As	1	0.24434(13)	0.34140(12)	0.14586(4)	0.0311(2)	0.0408(5)	0.0271(4)	0.0278(5)	−0.0070(3)	0.0124(4)	−0.0114(4)
Me3a	As	0.821(7)	0.7014(3)	0.65391(18)	0.04057(8)	0.0368(4)	0.0385(10)	0.0305(7)	0.0415(9)	−0.0058(5)	0.0075(8)	−0.0196(6)
Me3b	Sb	0.179(7)	0.6456(7)	0.6448(14)	0.0321(2)	0.076(3)	0.011(2)	0.188(9)	0.025(3)	0.003(3)	−0.0021(17)	−0.021(3)
As4	As	1	0.13740(10)	0.67888(12)	0.05724(4)	0.02696(18)	0.0210(4)	0.0361(5)	0.0252(4)	0.0013(3)	0.0077(3)	−0.0016(3)
Me5a	As	0.531(10)	0.4266(3)	0.0230(3)	0.0518(2)	0.0329(7)	0.0295(9)	0.0409(10)	0.0300(19)	0.0026(9)	0.0097(9)	−0.0061(7)
Me5b	Ag	0.469(10)	0.4147(3)	0.0130(3)	0.0769(2)	0.0460(9)	0.0419(11)	0.0633(13)	0.034(2)	−0.0015(11)	0.0113(10)	−0.0005(9)
Me6a	Pb	0.594(4)	0.90183(11)	0.08429(14)	0.07001(4)	0.0316(3)	0.0278(4)	0.0362(5)	0.0319(4)	0.0039(3)	0.0089(2)	0.0078(3)
Me6b	As	0.406(4)	0.8755(6)	0.0322(7)	0.0829(3)	0.0561(12)	0.064(3)	0.039(2)	0.073(3)	−0.0007(18)	0.034(2)	−0.0114(17)
S1	S	1	0.2558(3)	0.9955(3)	0.26374(10)	0.0315(5)	0.0254(10)	0.0263(10)	0.0437(13)	0.0045(9)	0.0087(9)	0.0026(8)

S2	S	1	0.2454(3)	0.4830(3)	0.22281(9)	0.0258(4)	0.0245(9)	0.0278(10)	0.0258(10)	−0.0077(8)	0.0063(8)	−0.0013(8)
S3	S	1	0.5086(2)	0.6867(3)	0.32823(10)	0.0273(4)	0.0189(9)	0.0253(9)	0.0381(12)	0.0005(8)	0.0065(8)	0.0037(7)
S4	S	1	0.8992(3)	0.1720(3)	0.17540(10)	0.0321(5)	0.0321(11)	0.0288(10)	0.0378(12)	−0.0010(9)	0.0123(9)	0.0011(9)
S5	S	1	0.6995(3)	0.8368(3)	0.11015(9)	0.0254(4)	0.0245(9)	0.0236(9)	0.0265(10)	0.0009(7)	0.0004(8)	−0.0009(7)
S6	S	1	0.1619(3)	0.8828(3)	0.12065(10)	0.0337(5)	0.0458(13)	0.0227(10)	0.0319(12)	0.0029(8)	0.0053(10)	−0.0028(9)
S7	S	1	0.3615(3)	0.5276(3)	0.09584(9)	0.0283(4)	0.0200(9)	0.0361(11)	0.0303(11)	−0.0005(8)	0.0087(8)	−0.0041(8)
S8	S	1	0.9567(3)	0.5110(3)	0.08664(15)	0.0460(7)	0.0303(12)	0.0229(10)	0.091(2)	0.0022(12)	0.0284(14)	−0.0010(9)
S9	S	1	0.5878(3)	0.1959(3)	0.01676(13)	0.0432(6)	0.0292(12)	0.0330(12)	0.0687(19)	0.0035(12)	0.0126(12)	−0.0034(10)
S10	S	1	0.1810(3)	0.1794(3)	0.01204(10)	0.0306(4)	0.0281(10)	0.0338(11)	0.0307(11)	0.0006(9)	0.0079(8)	−0.0055(9)

Table S2a. Bond lengths in sample rath3.

Pb1–		**Pb2–**		**As1–**		**As2–**		**As4–**	
S2	2.990(2)	S4	2.971(2)	S4	2.226(2)	S2	2.234(2)	S6	2.249(2)
S1	2.997(2)	S1	3.039(2)	S1	2.247(2)	S7	2.277(2)	S8	2.262(2)
S3	3.032(2)	S6	3.052(2)	S3	2.318(2)	S3	2.387(2)	S7	2.325(2)
S6	3.194(2)	S5	3.072(2)	S8	3.219(2)	S8	2.963(2)	S10	3.150(2)
S2	3.202(2)	S2	3.130(2)	S7	3.245(2)	S4	3.425(2)	S9	3.350(3)
S1	3.238(2)	S1	3.263(2)						
S7	3.246(2)	S8	3.325(2)						
S5	3.294(2)	S4	3.408(2)						
S3	3.454(2)	S2	3.428(2)						
As3–		**As5–**		**Ag5–**		**Pb6–**			
S5	2.260(2)	S9	2.255(3)	S10	2.718(3)	S4	2.814(2)		
S10	2.269(2)	S9	2.409(4)	S6	2.744(3)	S6	2.879(2)		
S8	2.663(3)	S10	2.483(3)	S5	2.754(3)	S10	2.959(2)		
S9	2.730(3)	S5	2.927(3)	S9	2.781(3)	S5	2.966(2)		
S7	3.442(2)	S6	3.260(3)	S9	2.788(3)	S9	2.978(2)		
				S3	2.789(3)	S10	3.144(2)		
						S8	3.388(2)		

Table S2b. Bond lengths in sample rath4.

Pb1–		**Pb2–**		**As1–**		**As2–**		**As4–**	
S2	2.987(3)	S4	2.972(3)	S4	2.228(3)	S2	2.236(3)	S6	2.247(3)
S1	3.003(3)	S1	3.044(3)	S1	2.246(3)	S7	2.275(3)	S8	2.264(3)
S3	3.032(3)	S6	3.047(3)	S3	2.316(3)	S3	2.402(3)	S7	2.322(3)
S6	3.195(3)	S5	3.075(3)	S8	3.218(3)	S8	2.940(3)	S10	3.148(3)
S2	3.202(3)	S2	3.124(3)	S7	3.247(3)	S4	3.416(3)	S9	3.353(3)
S1	3.227(3)	S1	3.256(3)						
S7	3.245(3)	S8	3.335(3)						
S5	3.296(3)	S4	3.415(3)						
S3	3.459(3)	S2	3.427(3)						
As3–		**As5–**		**Ag5–**		**Pb6–**			
S10	2.266(3)	S9	2.249(5)	S10	2.717(4)	S4	2.800(3)		
S5	2.266(3)	S9	2.418(5)	S6	2.737(4)	S6	2.877(3)		
S8	2.680(3)	S10	2.484(5)	S5	2.746(4)	S10	2.953(3)		
S9	2.715(4)	S5	2.915(5)	S3	2.772(4)	S5	2.963(3)		
S7	3.445(3)	S6	3.261(5)	S9	2.790(4)	S9	2.967(3)		
				S9	2.792(5)	S10	3.139(3)		
						S8	3.388(3)		

Table S2c. Bond lengths in sample rath5 (recalculated from Berlepsch et al. [2]).

Pb1–		**Pb2–**		**As1–**		**As2–**		**As4–**	
S2	3.022(3)	S4	2.973(2)	S4	2.232(3)	S2	2.238(3)	S6	2.253(3)
S3	3.050(3)	S1	3.048(3)	S1	2.246(3)	S7	2.285(3)	S8	2.260(3)
S1	3.072(3)	S6	3.063(3)	S3	2.312(2)	S3	2.407(2)	S7	2.317(3)
S1	3.198(3)	S2	3.094(3)	S8	3.261(3)	S8	2.948(3)	S10	3.152(3)
S2	3.215(3)	S5	3.117(3)	S7	3.265(3)	S4	3.429(3)	S9	3.389(3)
S6	3.221(2)	S1	3.202(3)						
S7	3.300(2)	S2	3.412(3)						
S5	3.347(3)	S8	3.451(3)						
S3	3.497(2)	S4	3.472(2)						

As3–		**Sb3–**		**As5–**		**Ag5–**		**Pb6–**		**As6–**	
S5	2.243(5)	S10	2.380(11)	S9	2.258(5)	S10	2.727(4)	S4	2.764(3)	S5	2.439(11)
S10	2.281(5)	S5	2.506(11)	S9	2.413(6)	S3	2.757(5)	S9	2.850(3)	S4	2.705(11)
S8	2.693(5)	S8	2.581(10)	S10	2.481(4)	S5	2.758(4)	S5	2.923(3)	S10	2.782(11)
S9	2.734(5)	S9	2.857(10)	S5	2.931(4)	S6	2.765(5)	S10	2.929(3)	S9	2.808(10)
S7	3.465(5)	S7	3.464(11)	S6	3.266(6)	S9	2.768(5)	S8	2.941(3)	S8	2.926(10)
		S9	3.528(11)			S9	2.841(5)	S8	3.138(3)		
								S8	3.427(3)		

Table S2d. Bond lengths in sample rath7.

Pb1–		**Pb2–**		**As1–**		**As2–**		**As4–**			
S2	3.025(2)	S4	2.981(3)	S1	2.238(3)	S2	2.231(2)	S6	2.253(3)		
S3	3.074(2)	S1	3.038(2)	S4	2.241(3)	S7	2.284(2)	S8	2.258(3)		
S1	3.106(2)	S2	3.055(2)	S3	2.311(2)	S3	2.414(2)	S7	2.306(3)		
S1	3.160(2)	S6	3.068(3)	S7	3.273(3)	S8	2.940(3)	S10	3.138(3)		
S2	3.222(2)	S1	3.159(3)	S8	3.285(3)	S4	3.427(3)	S9	3.386(3)		
S6	3.232(3)	S5	3.165(2)								
S7	3.319(2)	S2	3.384(2)								
S5	3.389(2)	S4	3.497(2)								
S3	3.505(2)	S8	3.548(3)								
As3–		**Sb3–**		**As5–**		**Ag5–**		**Pb6–**		**As6–**	
S10	2.232(3)	S10	2.439(8)	S9	2.230(5)	S10	2.670(4)	S4	2.733(3)	S5	2.343(7)
S5	2.272(3)	S5	2.456(9)	S9	2.433(5)	S9	2.713(6)	S6	2.831(3)	S4	2.543(6)
S8	2.528(4)	S9	2.476(7)	S10	2.473(3)	S3	2.721(5)	S9	2.890(3)	S6	2.714(6)
S9	2.865(4)	S8	2.938(7)	S5	2.906(4)	S6	2.783(5)	S5	2.912(3)	S10	2.880(5)
S7	3.566(3)	S7	3.264(7)	S3	3.227(6)	S5	2.786(3)	S10	2.930(3)	S9	2.984(6)
		S7	3.474(8)			S9	2.871(5)	S10	3.092(3)		
								S8	3.444(3)		

Table S3a. Polyhedron characteristics for atoms in sample rath3.

Site	Atom	Occ.	1	2	3	4	5	6	7	8	9	10
Pb1	(Pb,Tl)1	1	9	3.179	0.018	0.202	0.947	134.522	64.668	3.183	0.153	1.75
Pb2	(Pb,Tl)2	1	9	3.182	0.019	0.131	0.862	134.916	64.747	3.188	0.171	1.76
As1	As1	1	5	2.784	0.299	0.674	0.997	90.425	13.115	2.651	0.531	3.13
As2	As2	1	5	2.814	0.408	0.669	0.960	93.380	11.434	2.657	0.520	2.93
Me3	(As,Sb)3	0.90,0.10	5	2.896	0.465	0.672	0.934	101.776	11.260	2.673	0.482	2.63
As4	As4	1	5	2.828	0.334	0.683	0.982	94.697	13.042	2.667	0.538	3.01
Me5a	As5	0.546	5	2.751	0.270	0.554	0.980	87.179	13.161	2.667	0.415	2.46
Me5b	Ag5	0.454	6	2.762	0.059	0.030	0.976	88.256	26.436	2.762	0.028	1.15
Me6	(Pb,As)6	0.90,0.10	7	3.036	0.089	0.222	0.882	117.191	40.424	3.018	0.192	2.18

Notes: 1: coordination number, 2: radius r_s in Å of a circumscribed sphere least-squares fitted to the coordination polyhedron, 3: volume distortion υ = [V(ideal polyhedron)-V(real polyhedron)]/V(ideal polyhedron); the ideal polyhedron has the same number of ligands, 4: 'volume-based' eccentricity $ECC_V = 1-[(r_s-\Delta)/r_s]^3$; Δ is the distance between the center of the sphere and the central atom in the polyhedron, 5: 'volume-based' sphericity $SPH_V = 1-3\sigma_r r_s$; σ_r is the standard deviation of the radius r_s, 6: volume in $Å^3$ of the circumscribed sphere, 7: volume in $Å^3$ of coordination polyhedron, 8: average bond distance, 9: standard deviation of the bond distance, 10: bond-valence sum.

All values were calculated with IVTON (Balić Žunić & Vicković [29]; Makovicky & Balić Žunić [30]).

Table S3b. Polyhedron characteristics for atoms in sample rath4 (for explanation of header numbers see Table S3a).

Site	Atom	Occ.	1	2	3	4	5	6	7	8	9	10
Pb1	(Pb,Tl)1	1	9	3.178	0.018	0.203	0.948	134.493	64.646	3.183	0.154	1.75
Pb2	(Pb,Tl)2	1	9	3.182	0.020	0.132	0.861	135.015	64.770	3.188	0.173	1.76
As1	As1	1	5	2.786	0.300	0.675	0.996	90.581	13.119	2.651	0.532	3.13
As2	As2	1	5	2.809	0.404	0.663	0.958	92.890	11.450	2.654	0.511	2.91
Me3	(As,Sb)3	0.92,0.08	5	2.900	0.466	0.672	0.932	102.146	11.282	2.675	0.482	2.62
As4	As4	1	5	2.827	0.331	0.683	0.979	94.654	13.087	2.667	0.539	3.02
Me5a	As5	0.54	5	2.746	0.264	0.551	0.978	86.742	13.207	2.666	0.413	2.46
Me5b	Ag5	0.46	6	2.758	0.057	0.031	0.974	87.877	26.370	2.759	0.031	1.16
Me6	(Pb,As)6	0.87,0.13	7	3.030	0.089	0.223	0.878	116.477	40.152	3.012	0.195	2.22

Table S3c. Polyhedron characteristics for atoms in sample rath5 (calculated from Berlepsch et al. [2]) (for explanation of header numbers see Table S3a).

Site	Atom	Occ.	1	2	3	4	5	6	7	8	9	10
Pb1	(Pb,Tl)1	1	9	3.211	0.019	0.202	0.947	138.715	66.610	3.214	0.154	1.610
Pb2	(Pb,Tl)2	1	9	3.198	0.024	0.152	0.848	136.960	65.392	3.203	0.191	1.714
As1	As1	1	5	2.801	0.299	0.682	0.998	92.025	13.348	2.663	0.548	3.119
As2	As2	1	5	2.816	0.397	0.664	0.956	93.568	11.662	2.662	0.514	2.866
Me3a	As3	0.735	5	2.919	0.464	0.684	0.930	104.230	11.545	2.683	0.492	2.618
Me3b	Sb3	0.265	6	2.924	0.189	0.570	0.937	104.673	27.021	2.886	0.498	3.221
As4	As4	1	5	2.831	0.317	0.687	0.978	95.012	13.415	2.674	0.551	3.013
Me5a	As5	0.526	5	2.753	0.254	0.554	0.981	87.400	13.478	2.670	0.417	2.446
Me5b	Ag5	0.474	6	2.768	0.057	0.050	0.972	88.869	26.676	2.769	0.038	1.130
Me6a	Pb6	0.739	7	3.015	0.094	0.251	0.861	114.813	39.382	2.996	0.221	2.374
Me6b	As6	0.261	5	2.857	0.343	0.392	0.980	97.659	13.265	2.732	0.182	1.553

Table S3d. Polyhedron characteristics for atoms in sample rath7 (for explanation of header numbers see Table S3a).

Site	Atom	Occ.	1	2	3	4	5	6	7	8	9	10
Pb1	(Pb,Tl)1	1	9	3.225	0.019	0.207	0.948	140.461	67.396	3.226	0.156	1.56
Pb2	(Pb,Tl)2	1	9	3.204	0.028	0.180	0.838	137.786	65.517	3.211	0.211	1.71
As1	As1	1	5	2.810	0.299	0.685	0.998	92.961	13.465	2.670	0.557	3.11
As2	As2	1	5	2.808	0.383	0.663	0.955	92.745	11.834	2.659	0.513	2.88
Me3a	As3	0.821	5	2.916	0.470	0.704	0.925	103.892	11.388	2.693	0.550	2.76
Me3b	Sb3	0.179	6	3.044	0.269	0.649	0.891	118.161	27.480	2.841	0.455	3.39
As4	As4	1	5	2.821	0.305	0.683	0.977	94.037	13.517	2.668	0.549	3.05
Me5a	As5	0.531	5	2.761	0.307	0.567	0.964	88.199	12.639	2.654	0.403	2.52
Me5b	Ag5	0.469	6	2.760	0.060	0.120	0.968	88.032	26.341	2.757	0.071	1.18
Me6a	Pb6	0.594	7	2.996	0.100	0.258	0.845	112.692	38.366	2.976	0.233	2.53
Me6b	As6	0.406	5	2.831	0.349	0.478	0.981	95.084	12.798	2.693	0.257	1.88