Table 6. Selected bond distances in rowleyite.

V1–O2 (×2)	1.994(3)	Na–O5 (×6)	2.555(4)
V1–O3 (×2)	1.826(3)	Na–Cl1 (×2)	3.154(3)
V1–O4	1.618(4)	<Na–φ>	2.705
V1–Cl3	3.054(3)		
		*A*1–O1 (×2)	2.917(4)
V2–O1 (×2)	1.996(3)	*A*1–O3 (×2)	2.836(3)
V2–O3 (×2)	1.818(3)	*A*1–O4 (×2)	3.234(4)
V2–O5	1.601(4)	*A*1–O5	3.281(5)
V2–Cl3	2.997(3)	*A*1–O5 (×2)	3.349(4)
		*A*1–Cl1	3.354(4)
P–O1 (×2)	1.564(3)	*A*1–Cl2	3.305(4)
P–O2 (×2)	1.549(3)	<*A*1–φ>	3.147
<P–O>	1.557		
		*A*2–O3 (×4)	3.046(5)
X–*X* channel close approaches		*A*2–Cl1 (×2)	3.336(3)
*X*2–*X*5	1.87(3)	*A*2–Cl2 (×2)	3.241(3)
*X*2–*X*8	1.4(2)	<*A*2–φ>	3.167
*X*2–*X*8	2.2(3)		
*X*2–*X*10	1.85(2)	O–*X* approaches	
*X*3–*X*4	1.67(6)	O1–*X*1	2.927(4)
*X*3–*X*12	1.13(7)	O2–*X*3	2.91(3)
*X*4–*X*5	2.16(4)	O2–*X*4	2.414(3)
*X*4–*X*12	2.16(6)	O2–*X*5	3.35(3)
*X*6–*X*7	1.27(3)	O2–*X*7	3.18(2)
*X*7–*X*7	2.19(6)	O2–*X*12	2.41(4)
*X*7–*X*12	1.42(6)	O4–*X*1	3.219(9)
*X*8–*X*8	0.9(6)	O4–*X*9	2.77(3)
*X*8–*X*8	1.45(9)		
*X*8–*X*8	1.7(3)	Cl–*X* close approaches	
*X*8–*X*8	2.0(3)	Cl3–*X*6	0.98(2)
*X*8–*X*10	1.53(10)	Cl3–*X*7	1.96(2)
*X*8–*X*11	1.83(10)		
*X*11–*X*11	0.92(10)		
*X*11–*X*11	1.30(15)		

Table 7. Site assignments for rowleyite (*epfu* / *apfu* with *Z* = 16).

Site	Mult.[1]	SREF[2]	V	P	As	Na	NH_4	K	Cl	□	*epfu*[3]
V1	96g	138	6								138
V2	96g	138	6								138
P	96h	103.0(5)		5.28	0.72						103.0
Na	16c	11.9(3)				1					11
*A*1	96g	60.1(8)					4.49	1.51			60.1
*A*2	48f	29.9(5)					2.26	0.74			29.9
Cl1	32e	33.2(4)							2		34
Cl2	32e	33.6(4)							2		34
Cl3	48f	39.0(6)							2.29	0.71	38.9
*X*1	96g	51.8(1.2)									
*X*2	96g	17.6(1.7)									
*X*3	96g	55(3)									
*X*4	96g	22.9(1.5)									
*X*5	96g	38(3)									
*X*6	48f	6.7(8)									
*X*7	96g	12.6(1.2)				Σ = 290.3 *epfu*					
*X*8	192i	70(5)									
*X*9	32e	5.9(5)									
*X*10	32e	4.0(9)									
*X*11	48f	2.1(6)									
*X*12	96g	3.7(1.1)									
Σ			12	6		1	6.75	2.25	6.29	0.71	

[1] site multiplicity
[2] refined site-scattering (electrons per formula unit)
[3] assigned electrons per formula unit

Table 8. Bond valence analysis for the ordered sites in rowleyite. Values are in valence units (*vu*).

	V1[1]	V2[1]	P[2]	Na	*A*1[3]	*A*2[3]	Σ
O1		$0.59^{\times 2\downarrow}$	$1.19^{\times 2\downarrow}$		$0.12^{\times 2\downarrow}$		1.90
O2	$0.59^{\times 2\downarrow}$		$1.24^{\times 2\downarrow}$				1.83
O3	$0.93^{\times 2\downarrow}$	$0.95^{\times 2\downarrow}$			$0.15^{\times 2\downarrow}$	$0.08^{\times 4\downarrow}$	2.11
O4	1.63				$0.05^{\times 2\downarrow\rightarrow}$		1.73
O5		1.71		$0.13^{\times 6\downarrow}$	0.04 $0.04^{\times 2\downarrow\rightarrow}$		1.96
Cl1				$0.07^{\times 2\downarrow}$	$0.10^{\times 3\downarrow\rightarrow}$	$0.14^{\times 2\downarrow \times 3\rightarrow}$	0.79
Cl2					$0.04^{\times 3\rightarrow}$	$0.11^{\times 2\downarrow \times 3\rightarrow}$	0.45
Cl3	$0.09^{\times 2\rightarrow}$	$0.10^{\times 2\rightarrow}$					0.38
Σ	4.76	4.89	4.86	0.92	0.90	0.82	

Bond-valence parameters are from Brese and O'Keeffe (1991).
[1] using $(V^{5+}_{0.8}V^{4+}_{0.2})$
[2] using $(P_{0.88}As_{0.12})$
[3] using K