Ionic liquids and deep eutectic mixtures as new solvents for the synthesis of vanadium fluorides and oxyfluorides

Farida. H. Aidoudi*, Peter. J. Byrne, Pheobe. K. Allan, Simon. J.Teat, Philip Lightfoot and Russell.E. Morris

Supplementary material

S1

Selected Bond Lenghts (Å), Bond Valence Sums S_{ij} [1]and hydrogen bonds (Å) for compounds **4**, **5**, **6**, **7, 8 and 10.**

Bond	Bond length (Å)	S_{ij}	Atoms D, H, A	D (D.....A)	Atoms D, H, A	D (D.....A)
			$(HNH_2CH_3)_2VOF_4(H_2O)$ (**4**)			
V1—O1	1.601(5)	1.436	N2—H2A—F1	2.713(8)	N1—H3D—F4^{iii}	2.960(9)
V1—F2	1.919(4)	0.553	N2—H2B—F2^{i}	2.899(8)	N1—H3E—F4	2.793(8)
V1—F4	1.952(5)	0.506	N2—H2B—F3^{i}	2.981(8)	N1—H3F—F1^{iv}	2.862(8)
V1—F1	1.944(5)	0.517	N2—H2C—F4^{ii}	2.726(8)	OW—HW1—F3^{v}	2.655(7)
V1—F3	1.959(4)	0.497	N1—H3D—F3^{iii}	3.026(8)	OW—HW2—F2^{i}	2.689(7)
V1-- OW	2.266(5)	0.269	(i) 1-x, 1-y, -z; (ii) 1+x, y, z; (iii) -x, 1-y, 1-z; (iv) 1-x, 1-y, 1-z;			
		∑V1 = 3.77	(v) -x, 1-y, -z.			
			$(HNH_2CH_3)_4V_2O_2F_8$ (**5**)			
V1—O1	1.563(4)	1.592	N2—H2B—F3	2.664(6)	N4—H4C—F3^{iv}	2.931(6)
V1—F2	1.951(3)	0.507	N2—H2B—F8^{i}	2.809(6)	N4—H4A—F8^{v}	2.719(6)
V1—F2^{ii}	2.225(4)	0.242	N2—H2A—F5	2.735(6)	N4—H4A—F7^{v}	3.016(6)
V1—F1	1.928(3)	0.539	N2—H2C—F7^{ii}	2.691(6)	N4—H4B—F6^{vi}	2.705(5)
V1—F4	1.907(3)	0.572	N1—H1B—F5^{ii}	2.633(5)	N3—H3C—F1	2.671(6)
V1—F3	1.925(3)	0.544	N1—H1C—F4^{ii}	2.644(6)	N3—H3C—F4	2.955(5)
		∑V1= 4.00	N1—H1A—F1^{iii}	2.899(6)	N3—H3B—F8^{vii}	2.720(5)
V2—O2	1.588(4)	1.488	N1—H1A—F3	2.808(6)	N3—H3A—F2^{viii}	2.768(5)
V2—F7	1.896(3)	0.587	N1—H1A—F2	3.037(5)	N3—H3A—F4^{ix}	2.901(6)
V2—F5	1.913(3)	0.562	N4—H4C—F1^{i}	2.702(5)		
V2—F8	1.939(3)	0.524	(i) 1-x, 1-y, 2-z; (ii) 1+x, y, z; (iii) 2-x, 1-y, 3-z; (iv) -1+x, y, -1+z; (v) -x, 1-y, 1-z; (vi) x, y, -1+z; (vii) x, y, 1+z; (viii) -1+x, y, z; (ix) 1-x, 1-y, 3-z.			
V2—F6^{i}	1.971(3)	0.481				
V2—F6	2.178(3)	0.274				
(i) 1-x, 1-y, 2-z; (ii) 2-x, 1-y, 3-z.		**∑V2= 3.92**				
			$(HNH_2CH_3)_2VF_5$ (**6**)			
V1—F3	1.794(5)	0.780	N2—H2A—F3^{i}	2.867(9)	N1—H3A—F2	2.648(8)
V1—F3i	1.794(5)	0.780	N2—H2A—F2^{ii}	2.707(8)	N1—H3B—F3^{iv}	3.027(11)
V1—F1i	1.998(2)	0.449	N2—H2B—F3^{iii}	2.867(9)	N1—H3B—F3^{iii}	3.027(11)
V1—F1	1.998(2)	0.449	N2—H2B—F1^{iii}	3.039(12)	N1—H3C—F2^{v}	2.648(8)
V1—F2	2.082(6)	0.358	N2—H2C—F2	2.707(8)	N1—H3C—F3^{v}	3.279(11)
V1—F2i	2.082(6)	0.358	N1—H3C—F1^{vi}	3.277(12)		
i) -x, 1-y, 1-z		**∑V1 = 3.17**	(i) 0.5+x, 1.5-y, 0.5-z; (ii) x, 1.5-y, z; (iii) 0.5+x, y, 0.5-z; (iv) 0.5+x, 0.5-y, 0.5-z; (v) x, 0.5-y, z; (vi) -x, 1-y, 1-z.			
			$VF_3(H_2O)_2$ (**7**)			
V1—F2^{ii}	1.894 (9)	0.594	O1—H1—F2^{i}	2.636 (17)	O2—H4—F3^{iii}	2.653 (17)
V1—F2	1.894 (9)	0.594	O1—H2—F2^{ii}	2.661 (17)	O2—H3—F3^{iv}	2.663 (17)
V1—F1	1.937 (6)	0.529	-x, -y, 2-z; (ii) -x, -0.5+y, 1.5-z; (iii) x, 0.5-y, -0.5+z; (iv) x, y, -1+z			
V1—F1^{ii}	1.937 (6)	0.529				
V1—O2	2.034 (11)	0.462				
V1—O2^{ii}	2.034 (11)	0.462				
		∑V1= 3.17				
V2—F3^{i}	1.894 (9)	0.456				
V2—F3	1.894 (9)	0.456				
V2—F1^{i}	1.940 (6)	0.525				
V2—F1	1.940 (6)	0.525				
V2—O1^{i}	2.039 (11)	0.594				
V2—O1	2.039 (11)	0.594				
(i) 1-x, -y, 2-z; (ii) -x, -y, 1-z.		**∑V2= 3.15**				

α- $H_2NH_2(CH_2)_2NH_2)VOF_4$ (**8**)

V1—O2	1.608 (17)	1.599	N1—H1A—F3^{i}	3.097(3)	N3—H3A—F5^{v}	2.937(3)
V1—F4	1.915 (14)	0.561	N1—H1A—F2	3.103(2)	N3—H3A—F7^{vi}	3.047(2)
V1—F6	1.933(19)	0.533	N1—H1B—F8	2.875(3)	N3—H3B—F4^{i}	2.786(3)
V1—F2	1.939 (16)	0.523	N1—H1B—O1^{ii}	2.941(3)	N3—H3B—O2^{vii}	3.037(3)
V1—F3^{i}	1.989 (13)	0.459	N1—H1C—F3^{ii}	3.203(3)	N3—H3C—F7^{viii}	2.800(2)
V1—F3	2.285 (13)	0.204	N2—H2A—F7^{iii}	2.765 (3)	N4—H4A—F2	2.777(3)
		∑V1 = 3.88	N2—H2A—F5^{ii}	3.063(3)	N4—H4B—F4^{i}	2.852(3)
V2—O1	1.744 (18)		N2—H2B—O1^{ii}	2.850(3)	N4—H4B—O2^{vii}	3.144(3)
V2—F8	1.780 (18)		N2—H2B—F8	3.086(3)	N4—H4C—F6^{i}	2.685(2)
V2—F1	1.918 (19)		N2—H2C—F1	2.688(2)	N4—H4C—F8	3.039(3)
V2—F7	1.918(18)		N2—H2C—O2^{iv}	3.050(3)		
V2—F5	2.116 (15)					
V2—F5^{ii}	2.164 (14)					

(i) 1.5-x, 0.5+y, 0.5-z; (ii) x, 1+y, z; (iii) 2.5-x, 0.5+y, 0.5-z; (iv) 2-x, 1-y, 1-z; (v) -0.5+x, 0.5-y, -0.5+z; (vi) 2-x, 1-y, -z; (vii) 1.5-x, -0.5+y, 0.5-z; (viii) 2-x, -y, -z.

i) 1.5-x, 0.5+y, 0.5-z; **∑V2 = 3.63**
(ii) 2.5-x, 0.5+y, 0.5-z;
(iii) 1.5-x, -0.5+y, 0.5-z; (iv) 2.5-x, -0.5+y, 0.5-z.

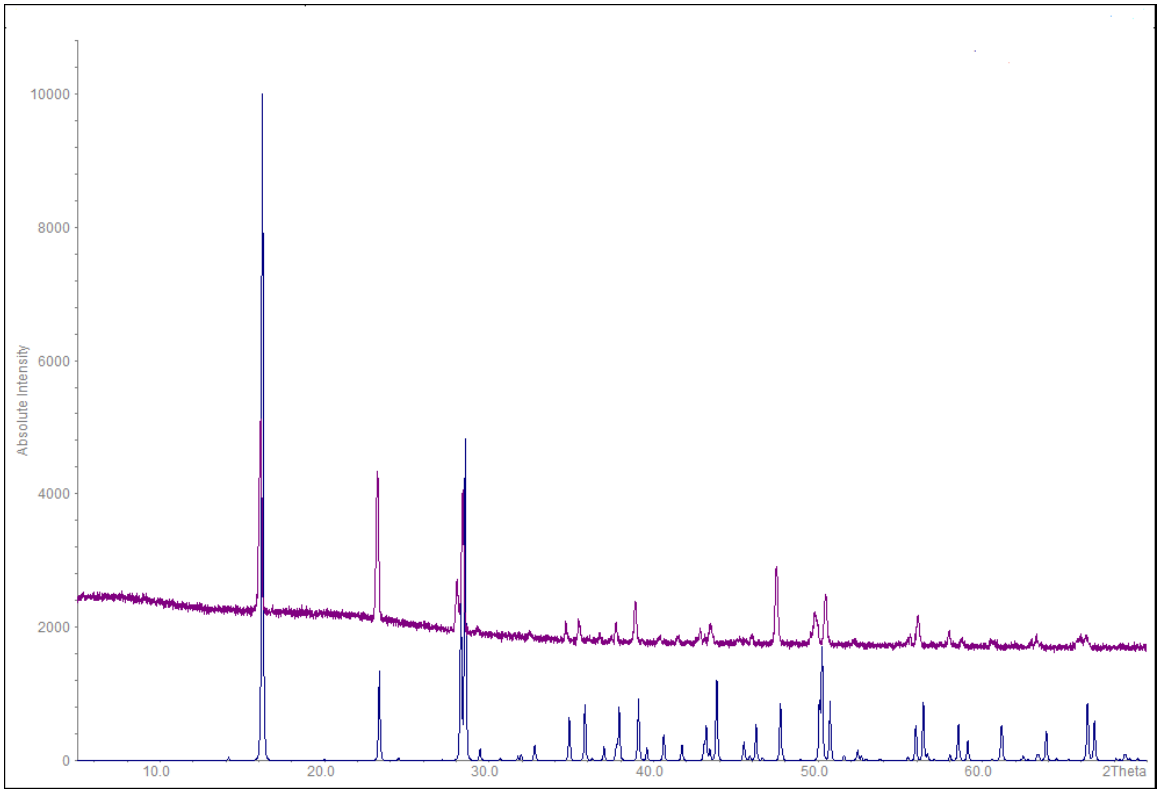
β-$H_2NH_2(CH_2)_2NH_2)VOF_4$ (**10**)

V1—O1	1.627(6)	1.338	N1—Hv1C—F2^{i}	2.654(5)
V1—F1^{viii}	1.917(3)	0.556	N1—H1D—F1^{ii}	2.811(5)
V1—F1^{ix}	1.917(3)	0.556	N1—H1E—F1^{iii}	2.748(5)
V1—F1	1.917(3)	0.556	N1—H1E—F1^{iv}	3.130(5)
V1—F1^{x}	1.917(3)	0.556	(i) -0.5+y, -x, 1-z; (ii) -.0.5+y, 0.5+x, 0.5-z; (iii) -x, 1-y, 1-z; (iv) -y, 0.5+x, 1-z.	
V1—O1^{xi}	2.388(6)	0.171		
		∑V1 = 3.73		
V2—O2ii	1.703(2)	1.090		
V2—F2iii	1.909(3)	0.568		
V2—F2i	1.909(3)	0.568		
V2—F2	1.912(3)	0.564		
V2—F2^{iv}	1.912(3)	0.564		
V2—O2	2.312(2)	0.240		
		∑V2 = 3.59		

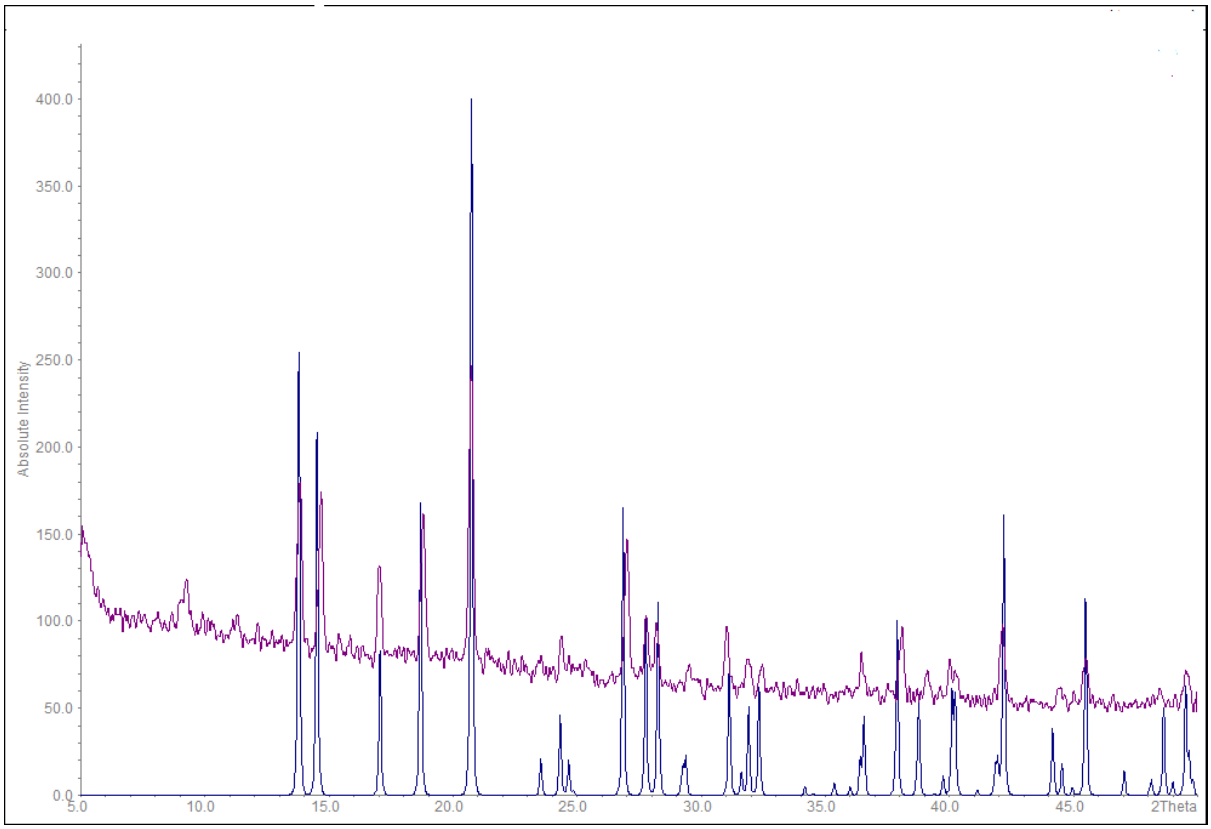
i) -y, -x, 0.5-z; (ii) -0.5-x, y, 0.5+z; (iii) -0.5+y, 0.5+x, 0.5-z; (iv) -0.5-x, 0.5-y, z;
(v) -0.5-x, y, -0.5+z; (vi) -0.5+y, -x, -z; (vii) -x, 1-y, 1-z;
(viii) y, 0.5-x, z;
(ix) 0.5-x, 0.5-y, z; (x) 0.5-y, x, z; (xi) 0.5-x, y, 0.5+z;
(xii) 0.5-x, y, -0.5+z.

1. N. E. Brese, M. O'keeffe. *Acta Crystallogr. Sect. B,* 1991, **47**, 192.

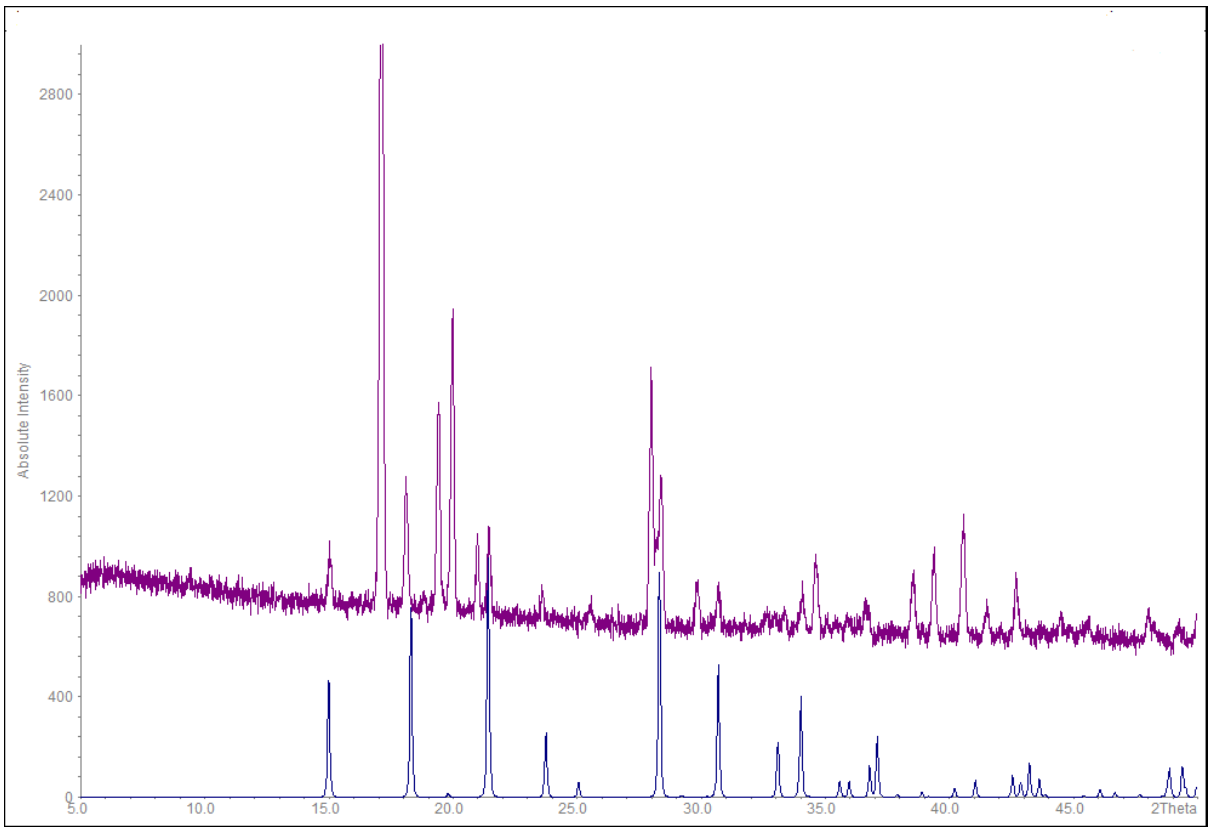
S2 Powder X ray diffraction for the experimental and calculated patterns for **1-10**



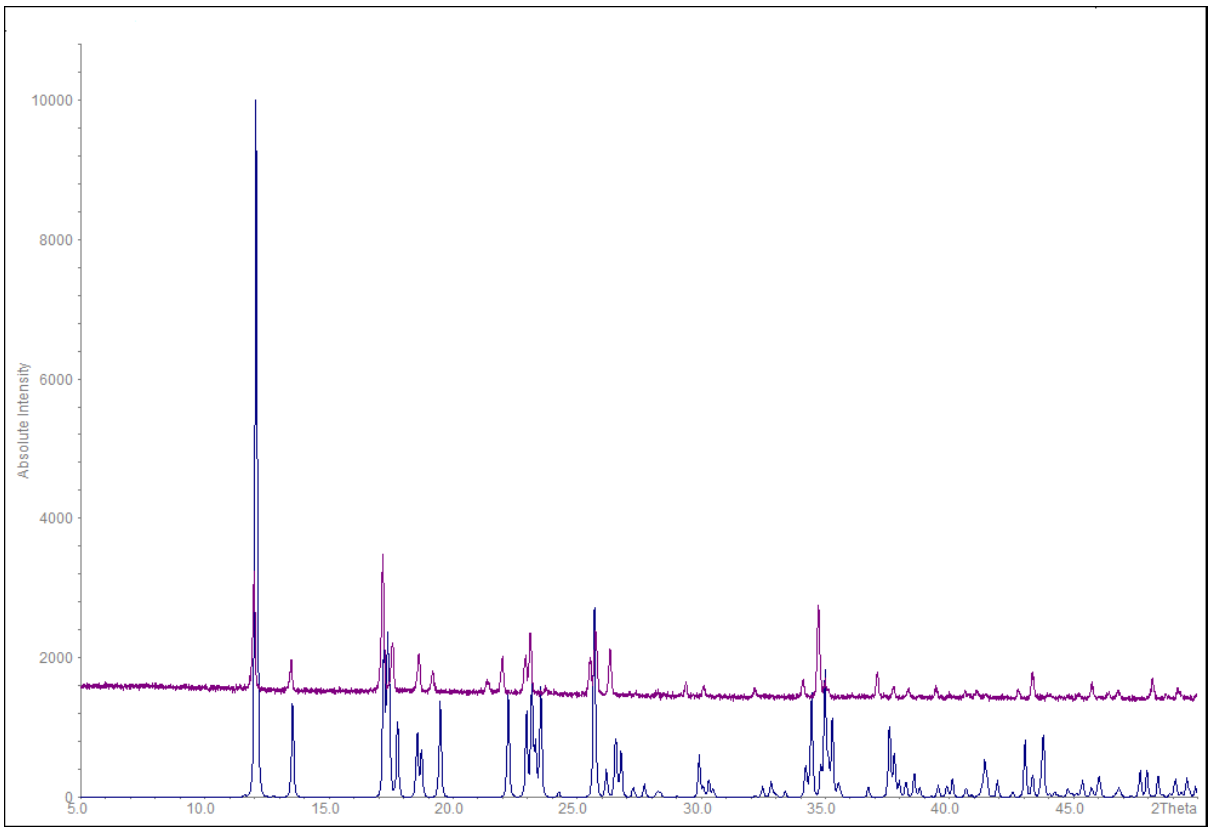
Experimental (above) and calculated (below) PXRD for **1**



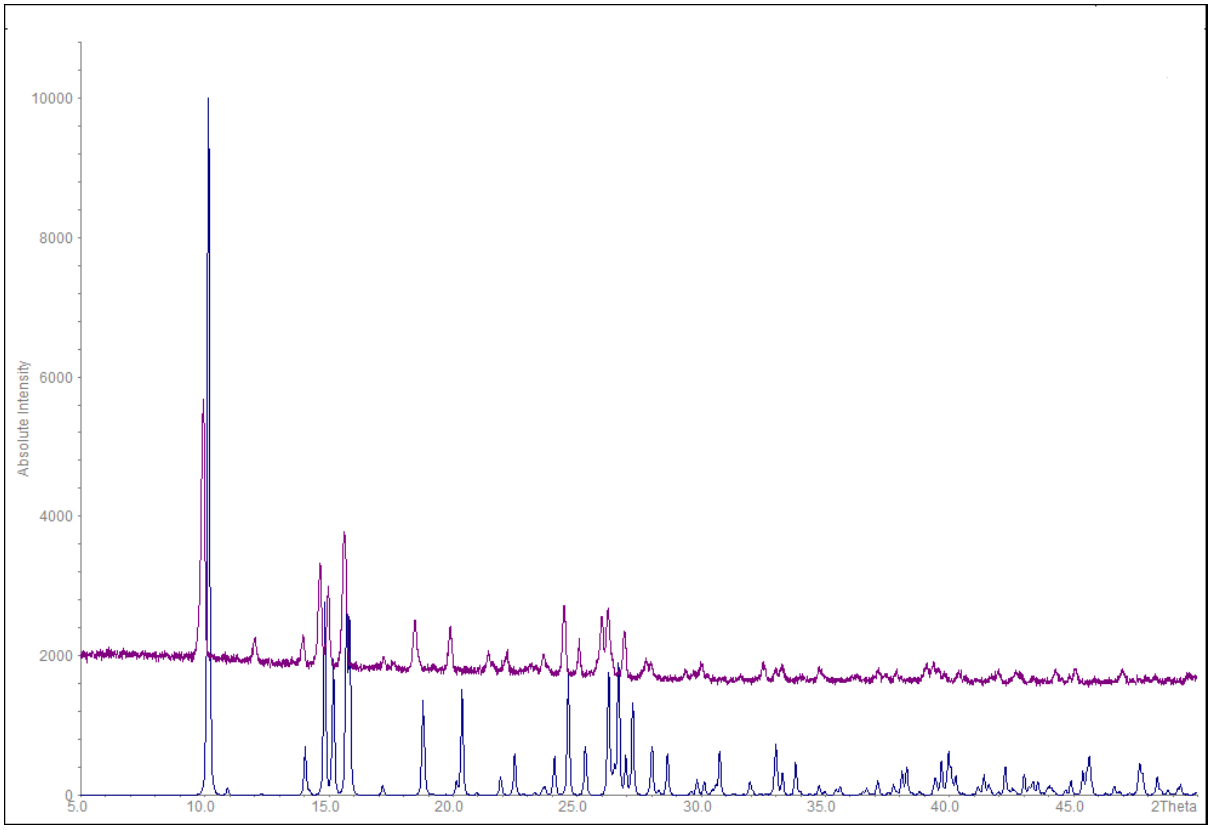
Experimental (above) and calculated (below) PXRD for **2**



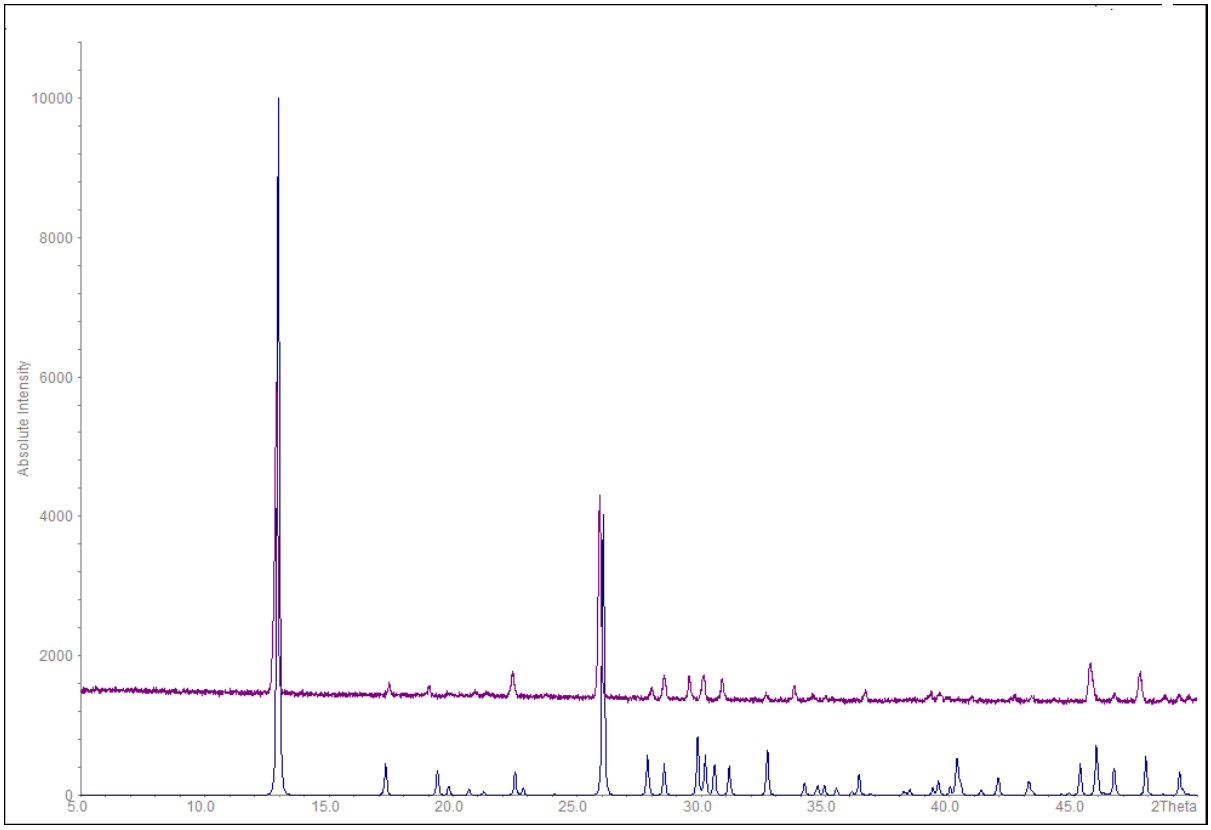
Experimental (above) and calculated (below) PXRD for **3**



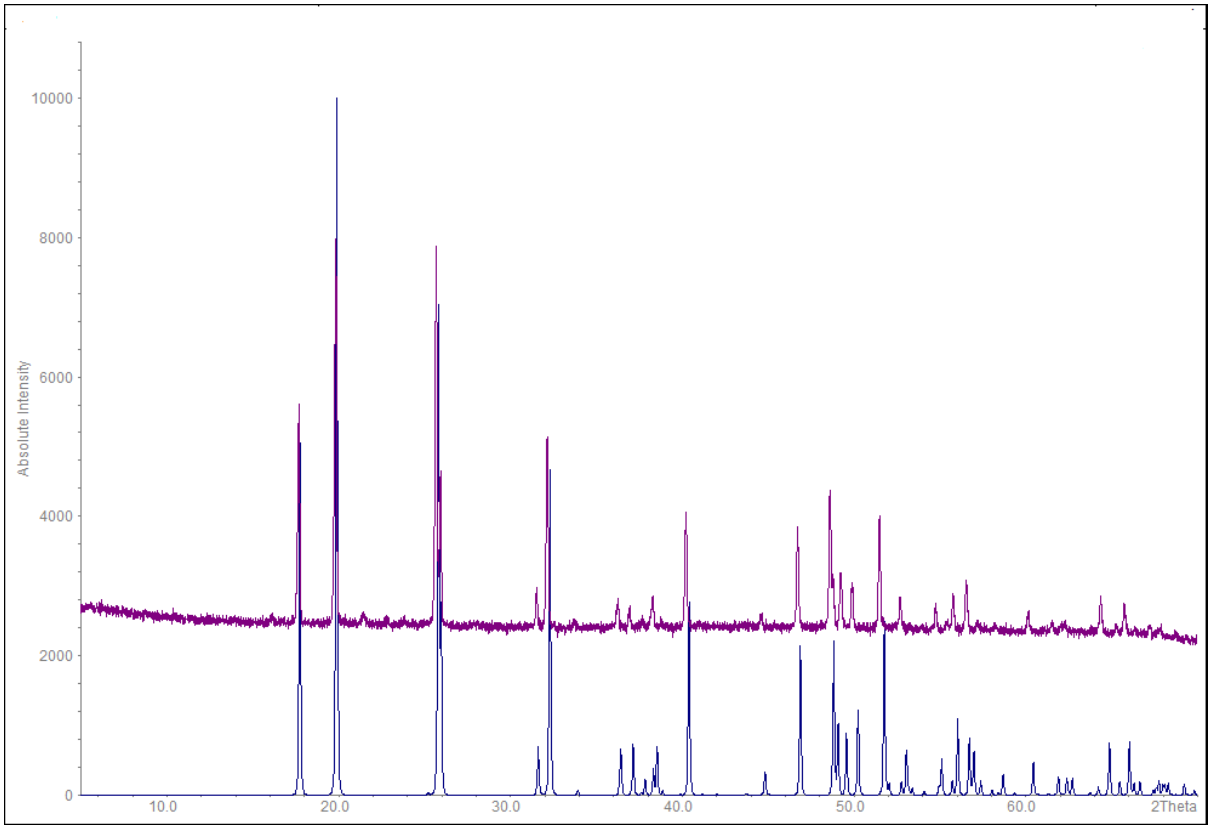
Experimental (above) and calculated (below) PXRD for **4**.



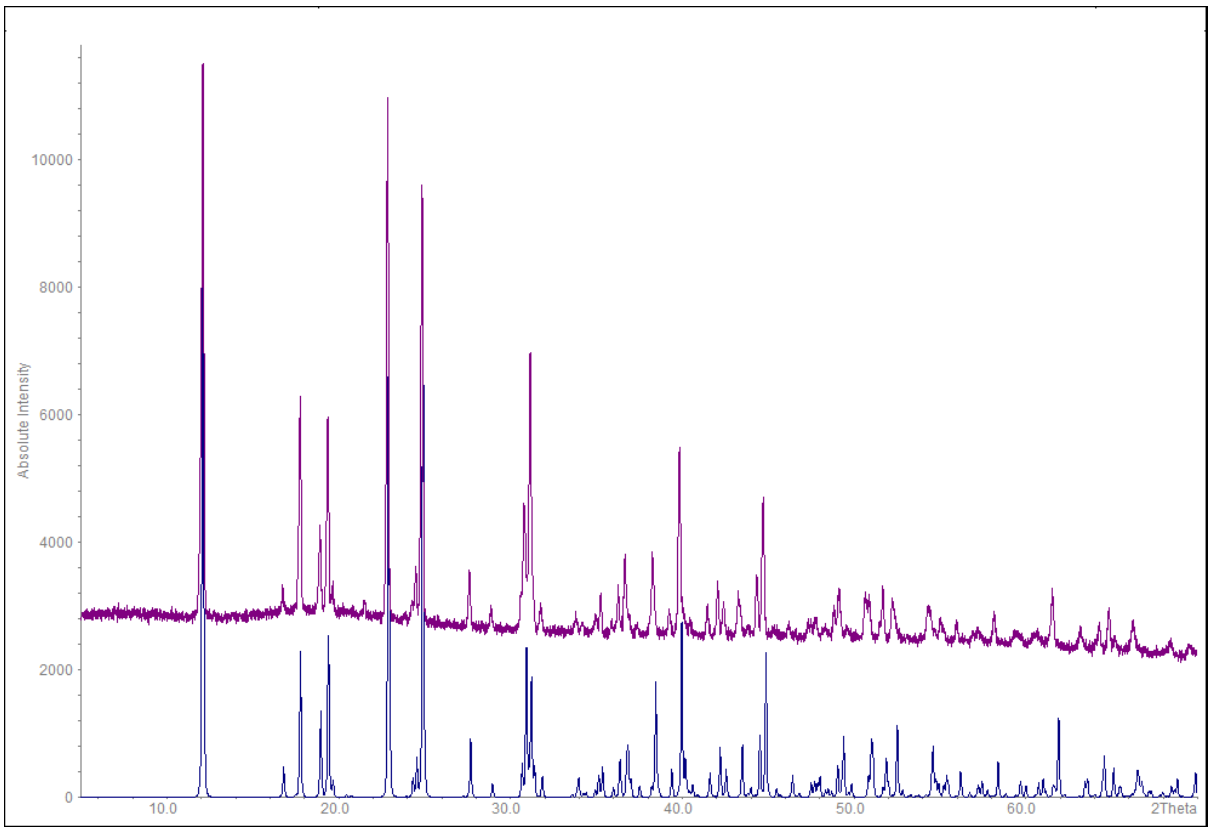
Experimental (above) and calculated (below) PXRD for **5.**



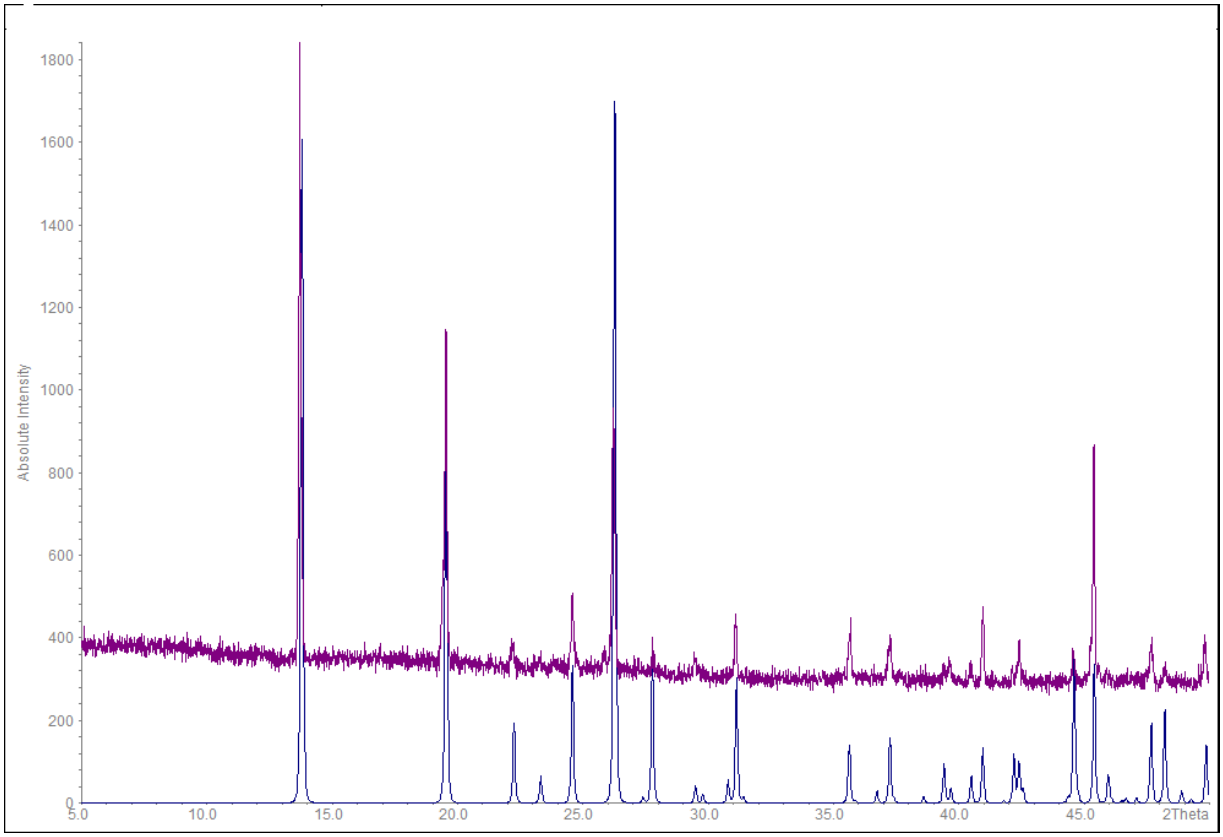
Experimental (above) and calculated (below) PXRD for **6**.



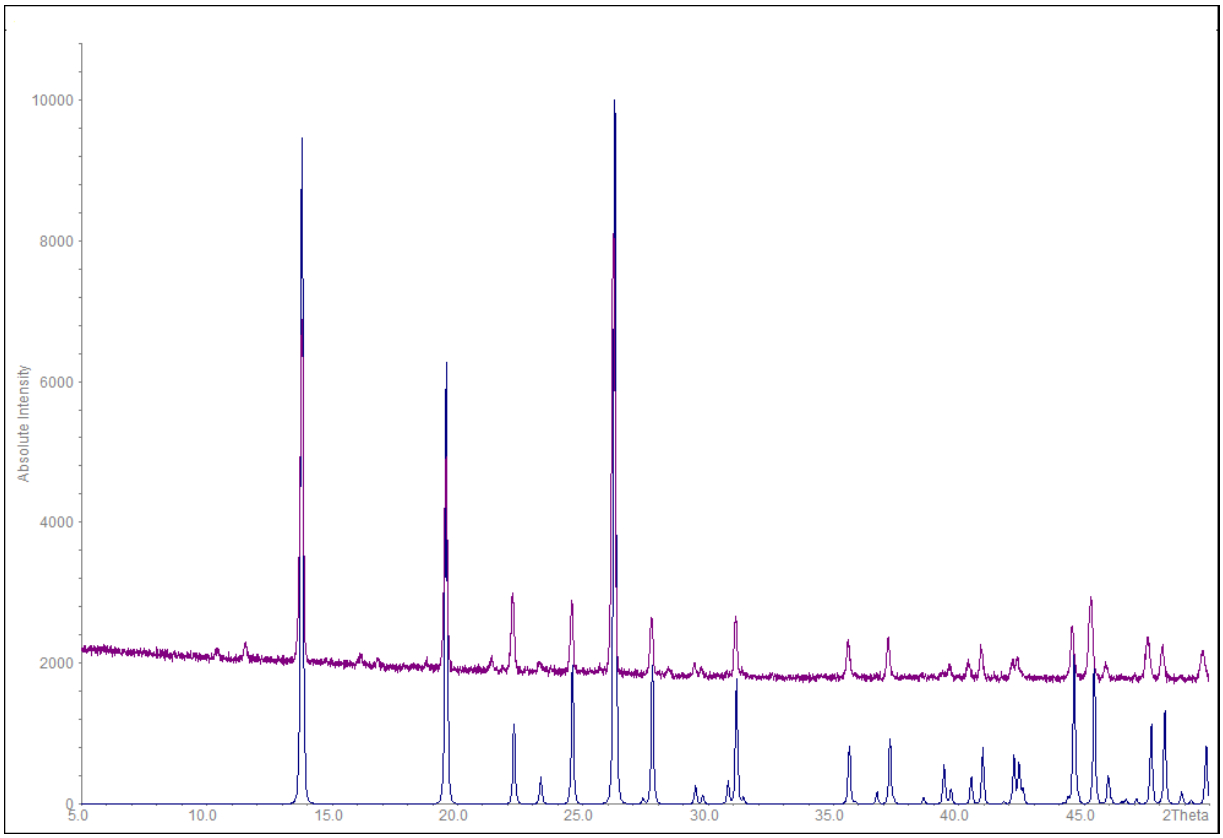
Experimental (above) and calculated (Below) PXRD for **7**.



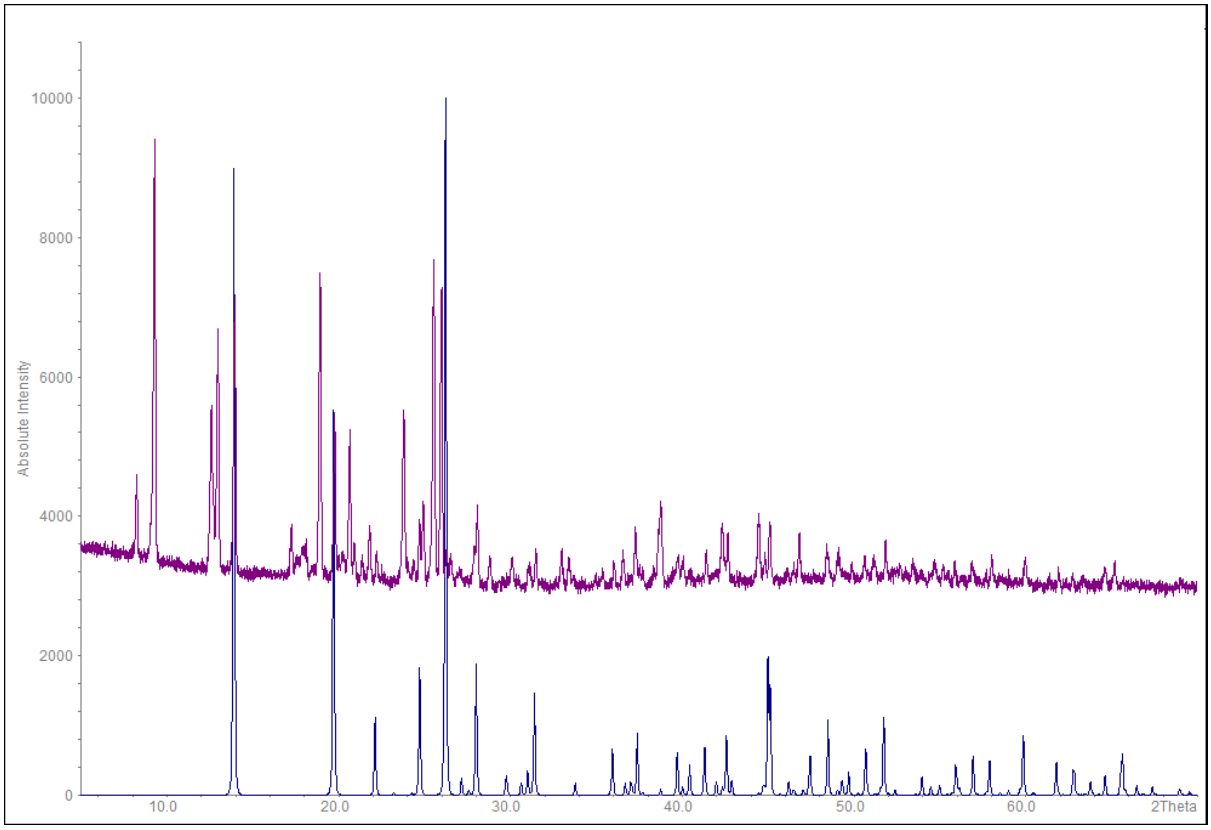
Experimental (above) and calculated (below) PXRD for **8**.



Experimental (above) and calculated (below) PXRD for **9a**.



Experimental (above) and calculated (below) PXRD for **9b**.



Experimental (above) and calculated (below) PXRD for **10**.