

# Neutral and cationic chelidonate coordination polymers with N,N'-bridging ligands

Rosa Carballo<sup>1,\*</sup>, Ana Belén Lago<sup>2,\*</sup>, Arantxa Pino-Cuevas<sup>1</sup>, Olaya Gómez-Paz<sup>1</sup>, Nuria Fernández-Hermida<sup>1</sup>, Ezequiel M. Vázquez-López<sup>1</sup>

<sup>1</sup> Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur (IISGS)-Universidade de Vigo, 36310 Vigo, Galicia, Spain; [rcrial@uvigo.es](mailto:rcrial@uvigo.es)

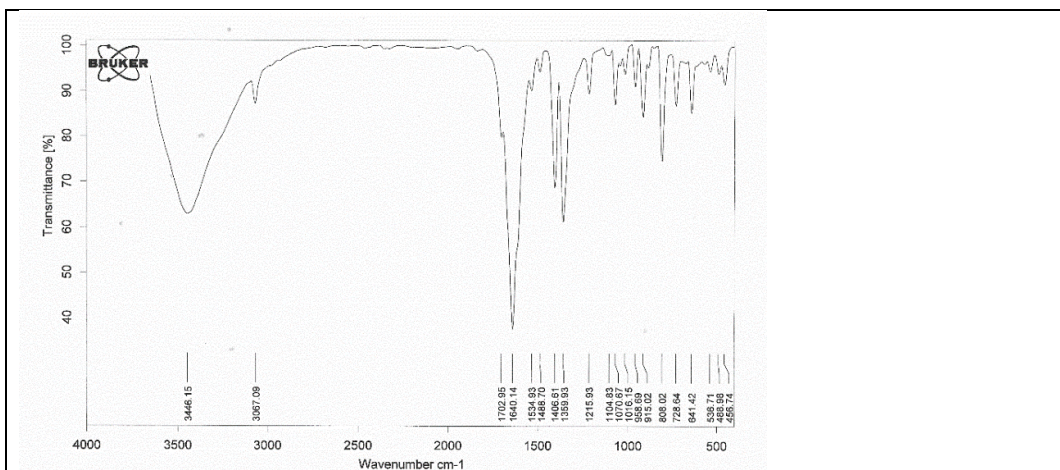
<sup>2</sup> Departamento de Química, Facultad de Ciencias, Sección Química Inorgánica, Universidad de la Laguna, 38206 La Laguna, Spain; [alagobla@ull.edu.es](mailto:alagobla@ull.edu.es)

\* Correspondence: [rcrial@uvigo.es](mailto:rcrial@uvigo.es) (R.C.) and [alagobla@ull.edu.es](mailto:alagobla@ull.edu.es) (A.B.L.)

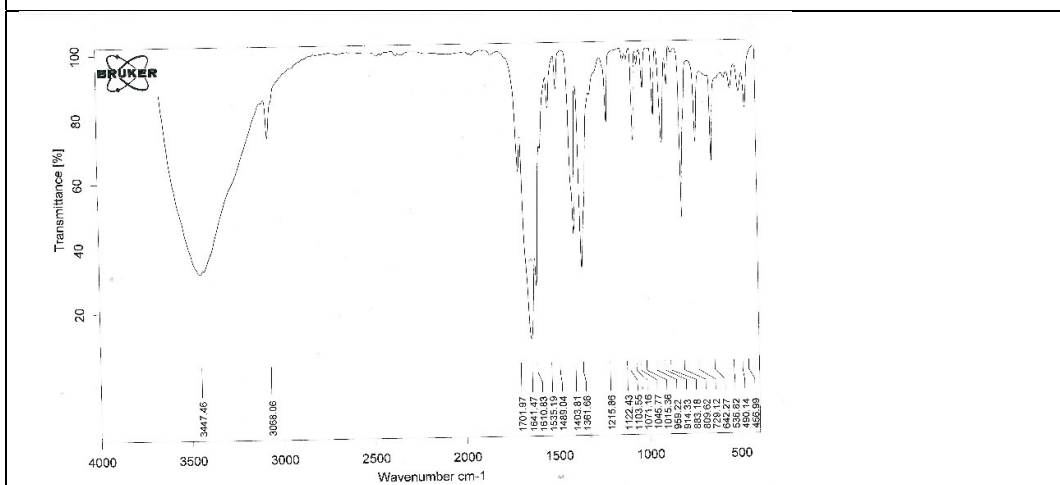
## Supplementary material

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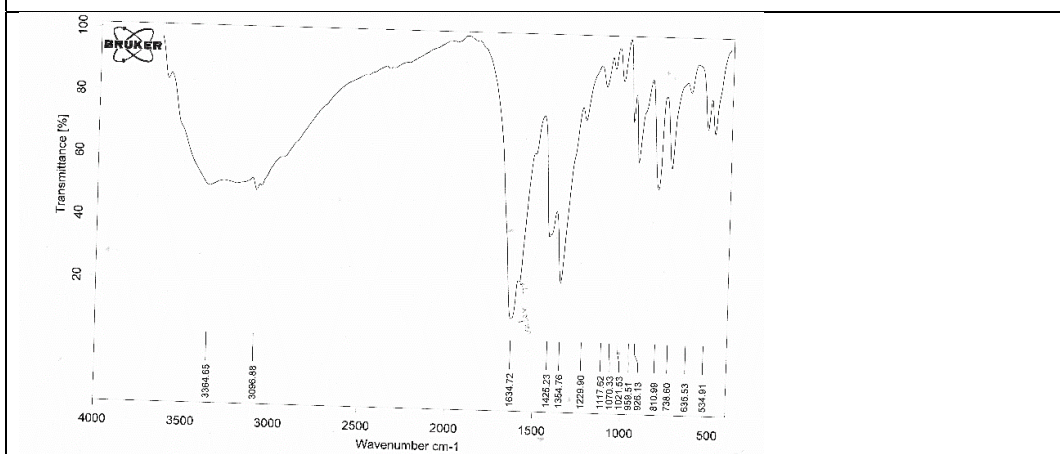
## IR spectra



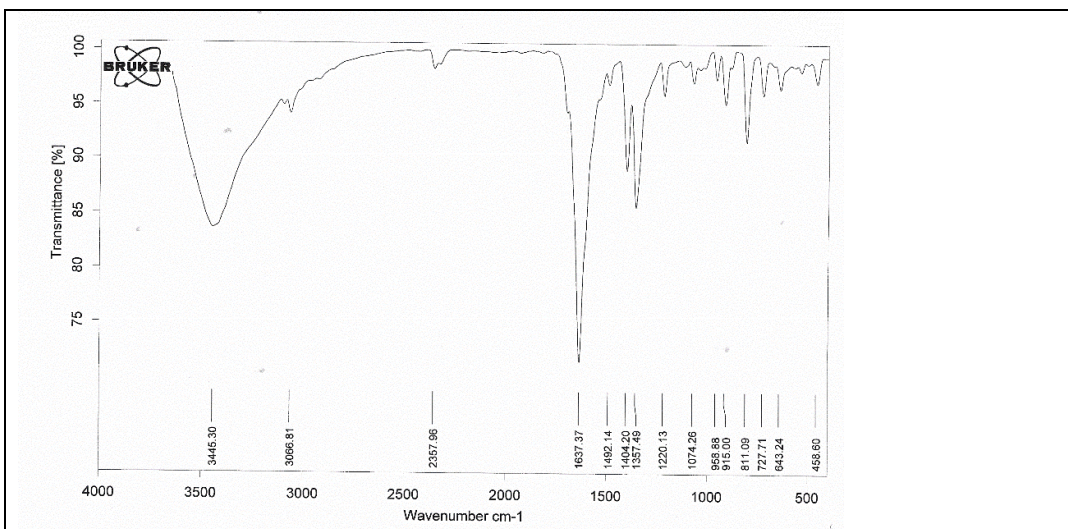
IR spectrum of  $2_{\infty}[\text{Zn}(\text{chel})(4,4\text{-bipy})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  (1)



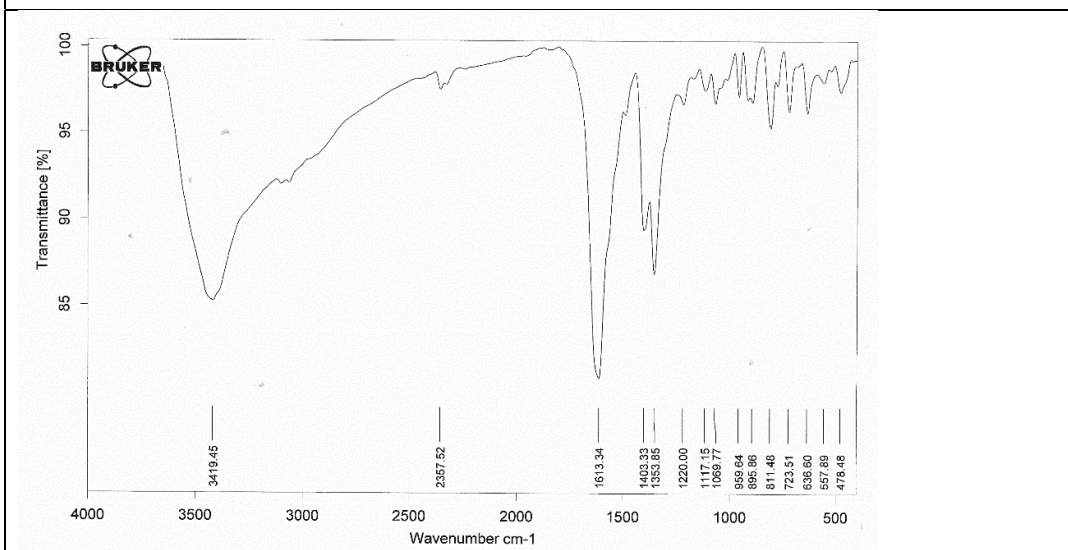
IR spectrum of  $1_{\infty}[\text{Zn}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel} \cdot 3\text{H}_2\text{O}$  (2)



IR spectrum of  $2_{\infty}[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  (3)



IR spectrum of  $1_{\infty}[\text{Cu}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 3\text{H}_2\text{O}$  (**4a**)



IR spectrum of  $1_{\infty}[\text{Cu}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 6\text{H}_2\text{O}$  (**4b**)

**Table 1S** Selected bond lengths/Å and angles/° in the cationic polymers [Zn(4,4-bipy)(H<sub>2</sub>O)<sub>4</sub>](chel)·3H<sub>2</sub>O (**2**), [Cu(4,4-bipy)(H<sub>2</sub>O)<sub>4</sub>](chel)·3H<sub>2</sub>O (**4a**) and [Cu(4,4-bipy)(H<sub>2</sub>O)<sub>4</sub>](chel)·6H<sub>2</sub>O (**4b**).

	<b>2</b>		<b>4a</b>		<b>4b</b>
Zn-O1	2.088(2)	Cu-O1	1.9524(18)	Cu-O1	2.028(2)
Zn-O2	2.105(2)	Cu-O2	2.417(2)	Cu-O2	2.032(2)
Zn-O3	2.102(2)	Cu-O1 <sup>i</sup>	1.9524(18)	Cu-O3	2.173(3)
Zn-O4	2.088(2)	Cu-O2 <sup>i</sup>	2.417(2)	Cu-O4	2.291(2)
Zn-N1	2.174(2)	Cu-N1	2.049(3)	Cu-N1	2.093(3)
Zn-N2	2.195(2)	Cu-N2	2.031(3)	Cu-N2 <sup>i</sup>	2.093(3)
O1-Zn-O2	176.28(11)	O1-Cu-O2	90.60(8)	O1-Cu-O2	177.21(9)
O1-Zn-O3	88.77(10)	O1 <sup>i</sup> -Cu-O1	176.45(13)	O1-Cu-O3	89.10(10)
O1-Zn-O4	92.53(10)			O1-Cu-O4	91.04(9)
O1-Zn-N1	88.75(8)	O1-Cu-N1	91.77(6)	O1-Cu-N1	89.89(10)
O1-Zn-N2	89.99(8)	O1-Cu-N2	88.23(6)	O1-Cu-N2 <sup>i</sup>	90.12(10)
N1-Zn-O2	91.76(9)	N1-Cu-O2	87.30(7)	N1-Cu-O2	89.63(9)
N2-Zn-O2	89.54(9)	N2-Cu-O2	92.70(7)	N2 <sup>i</sup> -Cu-O2	90.43(10)
O3-Zn-O2	87.57(10)	O1 <sup>i</sup> -Cu-O2	89.57(8)	O3-Cu-O2	88.26(9)
O3-Zn-N1	87.15(9)			O3-Cu-N1	91.58(10)
O3-Zn-N2	93.49(9)			O3-Cu-N2 <sup>i</sup>	90.01(10)
O2-Zn-O4	91.17(10)	O2-Cu-O2 <sup>i</sup>	174.59(15)	O2-Cu-O4	91.70(9)
O3-Zn-O4	174.83(10)			O3-Cu-O4	179.90(10)
N1-Zn-O4	87.88(9)			N1-Cu-O4	88.51(9)
N2-Zn-O4	91.51(9)			N2 <sup>i</sup> -Cu-O4	89.90(9)
N1-Zn-N2	178.58(8)	N1-Cu-N2	180.0	N1-Cu-N2 <sup>i</sup>	178.41(10)

i=-x-1, 2-y, z                      i=x,y+1,z

**Table 2S** Selected bond lengths/Å and angles/° in the neutral polymers <sup>2</sup><sub>∞</sub>[Zn(chel)(4,4-bipy)(H<sub>2</sub>O)]·2H<sub>2</sub>O (**1**) and <sup>2</sup><sub>∞</sub>[Zn(chel)(bpe)(H<sub>2</sub>O)]·H<sub>2</sub>O (**3**)

	<b>1</b>	<b>3</b>		<b>1</b>	<b>3</b>
Zn-O1W	2.032(3)	2.158(2)	O11-Zn-O1W	116.83(12)	84.32(10)
Zn-O11	2.015(3)	1.9781(17)	O11-Zn-O15	149.06(11)	83.32(7)
Zn-O15	2.539(3)	2.557(2)	O11-Zn-O14	93.59(12)	138.00(8)
Zn-O14	2.130(3)	2.0853(17)	O11-Zn-N1	94.84(13)	90.41(8)
Zn-N1	2.151(4)	2.147(2)	O11-Zn-N2	94.69(13)	123.85(9)
Zn-N2	2.157(3)	2.084(2)	O14-Zn-O15	55.51(10)	55.73(7)
			O14-Zn-N1	90.68(13)	92.71(8)
O1W-Zn-O15	93.95(11)	88.20(8)	O14-Zn-N2	85.31(13)	97.42(8)
O1W-Zn-O14	149.37(12)	85.38(10)	N1-Zn-O15	87.79(13)	82.37(8)
O1W-Zn-N1	90.23(14)	169.69(9)	N2-Zn-O15	82.27(12)	152.83(8)
O1W-Zn-N2	88.53(13)	94.08(9)	N1-Zn-N2	169.87(14)	96.21(9)

**Table 3S** Main hydrogen bonds in the cationic polymers [Cu(4,4-bipy)(H<sub>2</sub>O)<sub>4</sub>](chel)·3H<sub>2</sub>O (**4a**) [Cu(4,4-bipy)(H<sub>2</sub>O)<sub>4</sub>](chel)·6H<sub>2</sub>O (**4b**) and [Zn(4,4-bipy)(H<sub>2</sub>O)<sub>4</sub>](chel)·3H<sub>2</sub>O (**2**)

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
<b>4a</b>	O2W-H2WA...O13	0.69(4)	2.09(4)	2.781(3)	175(4)
	O1-H1A...O15 <sup>i</sup>	0.85(18)	1.82(2)	2.628(3)	158.5(16)
	O1-H1B...O1W <sup>ii</sup>	0.85(19)	1.81(11)	2.649(2)	170.5(2)
	O2W-H2WB...O15 <sup>iii</sup>	0.79(6)	2.13(6)	2.913(4)	169(5)
	O2-H2A...O2W	0.72(4)	2.08(4)	2.798(4)	172(4)
	O2-H2B...O14 <sup>iv</sup>	0.78(5)	2.18(5)	2.919(3)	160(4)
	O1W-H1WA...O14 <sup>v</sup>	0.85(13)	1.86(2)	2.688(3)	163.4(7)
i = 1/2+x, 3/2-y, -z; ii = -1/2+x, 1/2-y, -z; iii = -3/2-x, -1/2+y, -z; iv = x, y, 1+z; v = 1/2+x, 1/2-y, -z					
<b>4b</b>	O1-H1A...O11W	0.87(3)	1.81(4)	2.657(4)	161.7(2)
	O1-H1B...O13	0.87(2)	1.80(3)	2.661(3)	168.99(18)
	O2-H2B...O13W	0.88(2)	1.84(2)	2.687(3)	163.2(16)
	O2-H2A...O15 <sup>viii</sup>	0.88(2)	1.91(2)	2.688(3)	147.6(16)
	O3-H3A...O11W <sup>v</sup>	0.87(3)	1.86(4)	2.665(4)	152.2(2)
	O3-H3B...O12W	0.87(3)	1.89(2)	2.707(4)	155.5(2)
	O4-H4A...O13W <sup>vi</sup>	0.87(2)	1.88(2)	2.744(3)	171.1(2)
	O4-H4B...O14W <sup>iv</sup>	0.87(2)	1.95(3)	2.792(4)	160.8(2)
	O11W-H11A...O11 <sup>iv</sup>	0.87(3)	1.92(3)	2.775(4)	166.3(3)
	O11W-H11B...O14W <sup>iv</sup>	0.87(3)	1.99(3)	2.855(4)	175(2)
	O12W-H12A...O16W	0.87(3)	1.90(4)	2.729(5)	158.4(2)
	O12W-H12A...O12 <sup>i</sup>	0.87(3)	1.91(2)	2.748(4)	160.3(18)
	O13W-H13A...O13 <sup>v</sup>	0.87(2)	1.86(2)	2.721(3)	170.1(18)
	O13W-H13B...O15 <sup>v</sup>	0.87(2)	1.86(2)	2.723(3)	171.4(17)
	O14W-H14A...O14	0.87(2)	1.88(2)	2.742(3)	169.8(2)
	O14W-H14B...O14 <sup>ii</sup>	0.87(2)	2.06(2)	2.88(4)	155.9(18)
	O15W-H15A...O12	0.87(3)	1.97(3)	2.832(4)	169.5(2)
O15W-H15B...O16W	0.87(4)	1.89(5)	2.737(6)	165.8(3)	
O16W-H16B...O11 <sup>iii</sup>	0.87(6)	2.63(3)	2.889(5)	98.3(3)	
i = -x+1, -y+1, -z+1; ii = -x+2, -y+2, -z+2; iii = 1-x, 2-y, 1-z; iv = x, y-1, z; v = x-1, y, z; vi = x+1, y, z; vii = -x+1, -y+1, -z+2					
<b>2</b>	O3-H3A...O3W <sup>i</sup>	0.72(3)	1.96(4)	2.681(4)	177(4)
	O3-H3B...O16 <sup>ii</sup>	0.82(4)	1.97(4)	2.773(3)	165(4)
	O4-H4A...O2W <sup>iii</sup>	0.73(3)	2.04(3)	2.772(4)	173(4)
	O4-H4B...O1W <sup>iii</sup>	0.84(4)	1.83(4)	2.653(4)	169(4)
	O1-H1A...O14 <sup>v</sup>	0.78(4)	1.89(4)	2.663(3)	179(4)
	O1-H1B...O17 <sup>ii</sup>	0.74(3)	2.07(3)	2.803(3)	173(4)
	O2-H2A...O17	0.75(3)	2.05(3)	2.792(4)	170(3)
	O2-H2B...O16 <sup>vii</sup>	0.86(4)	1.93(4)	2.779(3)	171(3)
	O1W-H1WA...O14 <sup>iii</sup>	0.85(2)	1.94(2)	2.782(3)	173.8(18)
	O1W-H1WB...O17 <sup>iii</sup>	0.85(3)	2.03(2)	2.869(3)	172.2(16)
	O2W-H2WA...O15 <sup>vi</sup>	0.85(2)	1.95(2)	2.781(3)	166.1(2)
	O2W-H2WA...O15 <sup>iv</sup>	0.85(2)	2.12(3)	2.932(4)	159.8(18)
	O3W-H3WA...O13 <sup>ii</sup>	0.85(3)	1.93(2)	2.739(3)	157.5(2)
i = x, y-1, z; ii = x-1, y, z; iii = 1-x, -y, 1-z; iv = x-1, y, z-1; -z+2; v = -x+1, -y, -z+2; vi = 1-x, 1-y, 1-z; vii = -x+2, -y, -z+1					

**Table 4S** Main hydrogen bonds in the neutral polymers  ${}^2_{\infty}[\text{Zn}(\text{chel})(4,4\text{-bipy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  (**1**) and  ${}^2_{\infty}[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$  (**3**)

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
<b>1</b>	O(1W)-H(1WA)...O(15) <sup>i</sup>	0.85(3)	1.86(3)	2.699(4)	169.6(2)
	O(1W)-H(1WB)...O(12) <sup>ii</sup>	0.85(3)	1.95(4)	2.772(5)	163.6(3)
	O(2W)...O(13) <sup>iii</sup>			2.999(15)	
	i = -x+2, -y+1, -z+1; ii = -x+3, -y+1, -z+1; iii = x, 1+y, z				
<b>3</b>	O(1W)-H(1WA)...O(12) <sup>i</sup>	0.74(3)	2.03(3)	2.762(3)	171(4)
	O(1W)-H(1WB)...O(14) <sup>ii</sup>	0.76(3)	2.07(3)	2.825(3)	175(4)
	O(2W)-H(2WB)...O(3) <sup>iii</sup>	0.81(2)	2.34(3)	3.125(5)	164(10)
	i = -x+1, -y+2, -z+1; ii = -x+1, -y+2, -z; iii = x, y, z+1				

**Table 5S** Crystal data and structure refinement

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4a</b>	<b>4b</b>
Empirical formula	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>9</sub> Zn	C <sub>17</sub> H <sub>24</sub> N <sub>2</sub> O <sub>13</sub> Zn	C <sub>19</sub> H <sub>18</sub> N <sub>2</sub> O <sub>8</sub> Zn	C <sub>17</sub> H <sub>24</sub> N <sub>2</sub> O <sub>13</sub> Cu	C <sub>17</sub> H <sub>30</sub> N <sub>2</sub> O <sub>16</sub> Cu
Formula weight	457.70	529.75	467.72	527.92	581.97
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> -1
Unit cell dimensions					
<i>a</i> (Å)	9.9284(14)	7.4071(9)	9.9709(10)	13.0044(11)	7.1416(6)
<i>b</i> (Å)	11.1665(16)	11.4868(13)	21.169(2)	7.6275(6)	11.2903(10)
<i>c</i> (Å)	11.3456(16)	13.3024(15)	9.6111(10)	11.1758(9)	15.5056(13)
$\alpha$ (°)	109.793(2)	71.350(2)			78.390(2)
$\beta$ (°)	97.130(3)	82.415(2)	104.720(2)		82.081(2)
$\gamma$ (°)	113.343(2)	88.237(2)			83.412(2)
<i>V</i> (Å <sup>3</sup> )	1036.9(3)	1062.9(2)	1962.1(3)	1108.5(2)	1208.1(2)
<i>Z</i> / $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2 / 1.466	2 / 1.655	4 / 1.583	2 / 1.528	2 / 1.600
Absorption coeff. (mm <sup>-1</sup> )	1.234	1.229	1.302	1.056	0.986
<i>F</i> (000)	468	548	960	546	606
Crystal size (mm)	0.16x0.19x0.31	0.16x0.18x0.30	0.12x0.21x0.50	0.49x0.36x0.31	0.43x0.37x0.18
$\theta$ Range (°)	1.999 - 27.980	1.871 - 28.021	1.924 - 27.984	2.403 - 28.020	1.350 - 28.007
Reflections collected	6775	6958	12516	6976	7885
Indep. Reflections ( <i>R</i> <sub>int</sub> )	4717 (0.0314)	4851 (0.0244)	4626 (0.0710)	2601 (0.0238)	5521 (0.0199)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.061	1.001	0.794	1.029	1.051
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0561 w <i>R</i> 2 = 0.1517	<i>R</i> 1 = 0.0393 w <i>R</i> 2 = 0.0844	<i>R</i> 1 = 0.0410 w <i>R</i> 2 = 0.0581	<i>R</i> 1 = 0.0277 w <i>R</i> 2 = 0.0637	<i>R</i> 1 = 0.0464 w <i>R</i> 2 = 0.1245