Supplemental Material

Structures and Properties of Three Polymorphic Modifications based on Tetrahedral Building Blocks of Dichloro-bis(pyridazine-N) zinc(II)

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Details of the structure determination of form **I**

Details of the structure determination of form **II**

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Experimental X-ray powder pattern of form **I** and theoretical pattern calculated from single crystal data

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Experimental X-ray powder pattern of form **III** and theoretical pattern calculated from single crystal data

IR (top) and Raman (bottom) spectra for form **I**

IR (top) and Raman (bottom) spectra for form **II**

IR (top) and Raman (bottom) spectra for form **III**

Table 1. Crystal data and structure refinement for form I

Identification code	blz11	
Empirical formula	$C_8H_8Cl_2N_4Zn$	
Formula weight	296.45	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	Cc	
Unit cell dimensions	a = 14.0339(12) Å	α= 90°.
	b = 9.2082(5) Å	β= 100.579(9)°.
	c = 8.9873(7) Å	γ = 90°.
Volume	1141.66(15) $Å^3$	
Z	4	
Density (calculated)	1.725 Mg/m^3	
Absorption coefficient	2.590 mm^{-1}	
F(000)	592	
Crystal size	0.07 x 0.1 x 0.13 mm^3	
Theta range for data collection	2.66 to 28.00°.	
Index ranges	-18<=h<=18, -11<=k<=12, -11<=l<=11	
Reflections collected	5399	
Independent reflections	2547 [R(int) = 0.0267]	
Completeness to theta = 28.00°	96.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2547 / 2 / 137	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0583	
R indices (all data)	R1 = 0.0283, wR2 = 0.0595	
Absolute structure parameter	-0.004(11)	
Extinction coefficient	0.0100(6)	
Largest diff. peak and hole	0.292 and -0.467 e.$Å^{-3}$	

Remarks:

All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined isotropic (U_{eq}= -1.2) using a riding model with C-H = 0.95 Å for aromatic hydrogen atoms. There is one crystallographically independent molecules into the asymmetric unit, located at a general positions.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	4616(1)	7397(1)	3407(1)	17(1)
Cl(1)	3562(1)	7760(1)	1270(1)	25(1)
Cl(2)	5727(1)	9103(1)	4080(1)	33(1)
N(1)	5250(2)	5395(2)	3377(3)	18(1)
N(2)	5935(2)	5366(3)	2509(3)	28(1)
C(1)	6388(2)	4114(3)	2387(4)	30(1)
C(2)	6205(2)	2847(3)	3135(4)	29(1)
C(3)	5520(2)	2904(3)	4020(4)	30(1)
C(4)	5041(2)	4226(3)	4102(4)	21(1)
N(11)	3849(2)	7332(2)	5148(3)	19(1)
N(12)	3304(2)	6135(2)	5175(3)	24(1)
C(11)	2768(2)	6051(3)	6241(4)	27(1)
C(12)	2728(2)	7125(4)	7322(4)	30(1)
C(13)	3293(2)	8325(3)	7260(4)	31(1)
C(14)	3854(2)	8387(3)	6143(4)	24(1)

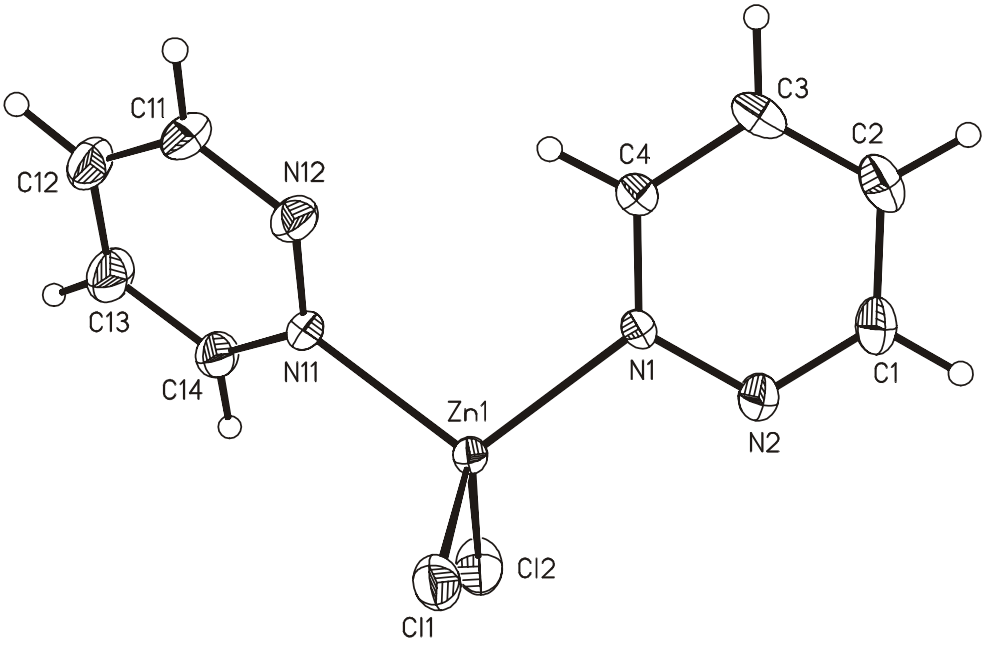

Table 3. Bond lengths [Å] and angles [°] .

Zn(1)-N(1)	2.049(2)	N(1)-Zn(1)-Cl(2)	110.81(7)
Zn(1)-N(11)	2.056(2)	N(11)-Zn(1)-Cl(2)	104.66(7)
Zn(1)-Cl(2)	2.2180(7)	N(1)-Zn(1)-Cl(1)	110.21(7)
Zn(1)-Cl(1)	2.2240(8)	N(11)-Zn(1)-Cl(1)	107.68(7)
N(1)-Zn(1)-N(11)	105.87(9)	Cl(2)-Zn(1)-Cl(1)	116.85(3)
C(14)-N(11)-Zn(1)	123.74(19)	C(4)-N(1)-Zn(1)	126.25(19)
N(12)-N(11)-Zn(1)	114.61(18)	N(2)-N(1)-Zn(1)	112.59(17)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	19(1)	12(1)	22(1)	0(1)	10(1)	1(1)
Cl(1)	29(1)	26(1)	22(1)	-1(1)	7(1)	8(1)
Cl(2)	27(1)	21(1)	54(1)	-9(1)	17(1)	-8(1)
N(1)	18(1)	13(1)	23(1)	1(1)	8(1)	3(1)
N(2)	29(1)	22(1)	38(2)	2(1)	20(1)	4(1)
C(1)	26(1)	30(2)	39(2)	-1(1)	16(1)	8(1)
C(2)	30(2)	22(1)	34(2)	-3(1)	5(1)	10(1)
C(3)	38(2)	15(1)	38(2)	3(1)	9(1)	3(1)
C(4)	24(1)	16(1)	26(2)	0(1)	10(1)	1(1)
N(11)	20(1)	19(1)	19(1)	2(1)	10(1)	2(1)
N(12)	25(1)	21(1)	30(2)	-1(1)	13(1)	-4(1)
C(11)	22(1)	29(2)	31(2)	4(1)	12(1)	-4(1)
C(12)	29(2)	39(2)	26(2)	6(1)	14(1)	6(1)
C(13)	37(2)	31(2)	28(2)	-6(1)	16(1)	0(1)
C(14)	31(2)	20(1)	25(2)	-4(1)	12(1)	0(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$).

	x	y	z	U(eq)
H(1)	6862	4083	1756	36
H(2)	6547	1975	3028	35
H(3)	5370	2076	4564	36
H(4)	4550	4284	4700	25
H(11)	2385	5204	6271	32
H(12)	2329	7028	8063	36
H(13)	3301	9097	7964	37
H(14)	4254	9212	6092	29

Table 2. Crystal data and structure refinement for form II

Identification code	gb175a	
Empirical formula	$C_8H_8Cl_2N_4Zn$	
Formula weight	296.45	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/C$	
Unit cell dimensions	a = 8.0254(5) Å	α= 90°.
	b = 16.9729(16) Å	β= 5.619(8)°.
	c = 8.5260(6) Å	γ = 90°.
Volume	1155.78(15) $Å^3$	
Z	4	
Density (calculated)	1.704 Mg/m^3	
Absorption coefficient	2.558 mm^{-1}	
F(000)	592	
Crystal size	0.08 x 0.14 x 0.22 mm^3	
Theta range for data collection	2.40 to 27.97°.	
Index ranges	-10<=h<=10, -22<=k<=21, -10<=l<=11	
Reflections collected	6630	
Independent reflections	2692 [R(int) = 0.0348]	
Completeness to theta = 27.97°	96.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2692 / 0 / 137	
Goodness-of-fit on F^2	0.797	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0932	
R indices (all data)	R1 = 0.0396, wR2 = 0.0994	
Extinction coefficient	0.023(3)	
Largest diff. peak and hole	0.742 and -0.862 $e.Å^{-3}$	

Remarks:

All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined isotropic (U_{eq}= -1.2) using a riding model with C-H = 0.95 Å for aromatic hydrogen atoms. There is one crystallographically independent molecules into the asymmetric unit, located at a general positions.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 0^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	7656(1)	6019(1)	7148(1)	17(1)
Cl(1)	9644(1)	6691(1)	8569(1)	26(1)
Cl(2)	6542(1)	4975(1)	8189(1)	26(1)
N(1)	8320(2)	5702(1)	4979(2)	17(1)
N(2)	9423(3)	6189(1)	4389(2)	25(1)
C(1)	9740(3)	6072(2)	2915(3)	30(1)
C(2)	8998(3)	5483(2)	1945(3)	29(1)
C(3)	7881(3)	4994(2)	2570(3)	28(1)
C(4)	7580(3)	5127(1)	4122(3)	22(1)
N(11)	5905(2)	6870(1)	6432(2)	18(1)
N(12)	4282(2)	6668(1)	6298(3)	27(1)
C(11)	3168(3)	7219(2)	5840(3)	31(1)
C(12)	3586(3)	7990(2)	5508(3)	29(1)
C(13)	5243(3)	8187(2)	5625(3)	30(1)
C(14)	6382(3)	7595(1)	6104(3)	27(1)

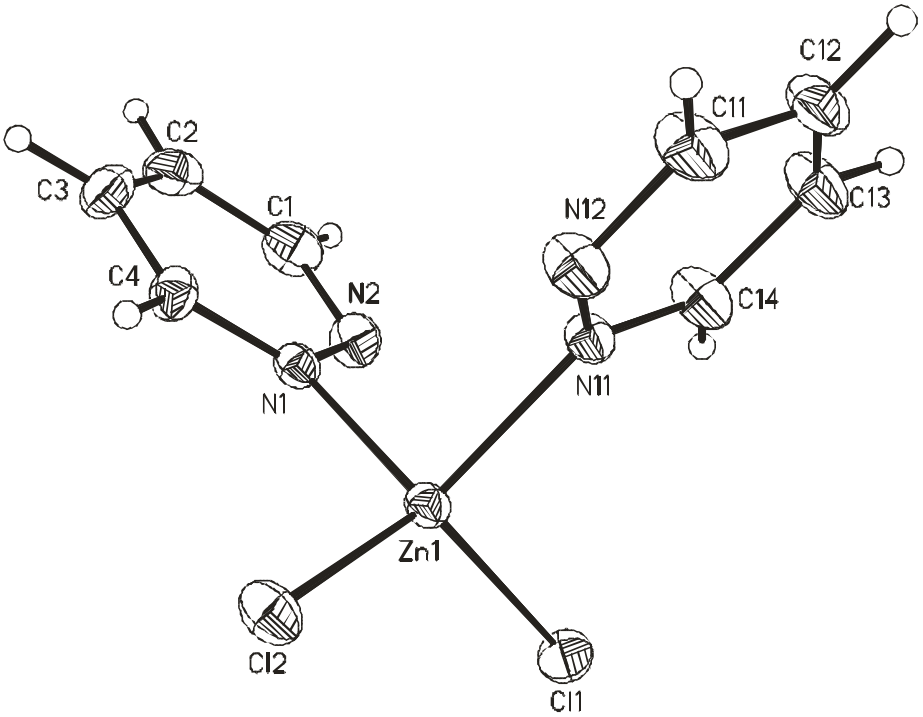

Table 3. Bond lengths [Å] and angles [°]

Zn(1)-N(1)	2.0462(19)	N(1)-Zn(1)-N(11)	98.43(7)
Zn(1)-N(11)	2.0654(17)	N(1)-Zn(1)-Cl(2)	107.68(5)
Zn(1)-Cl(2)	2.2092(6)	N(11)-Zn(1)-Cl(2)	112.89(5)
Zn(1)-Cl(1)	2.2211(6)	N(1)-Zn(1)-Cl(1)	113.04(5)
Cl(2)-Zn(1)-Cl(1)	119.32(2)	N(11)-Zn(1)-Cl(1)	103.53(5)
C(4)-N(1)-Zn(1)	123.40(16)	C(14)-N(11)-Zn(1)	120.61(15)
N(2)-N(1)-Zn(1)	114.57(14)	N(12)-N(11)-Zn(1)	118.24(14)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	15(1)	15(1)	19(1)	1(1)	0(1)	1(1)
Cl(1)	21(1)	26(1)	29(1)	-4(1)	-7(1)	-2(1)
Cl(2)	26(1)	22(1)	31(1)	8(1)	5(1)	-3(1)
N(1)	15(1)	17(1)	20(1)	2(1)	1(1)	1(1)
N(2)	27(1)	21(1)	27(1)	3(1)	4(1)	-7(1)
C(1)	30(1)	32(1)	28(1)	8(1)	8(1)	-1(1)
C(2)	29(1)	37(1)	21(1)	1(1)	2(1)	12(1)
C(3)	26(1)	31(1)	25(1)	-9(1)	-2(1)	3(1)
C(4)	20(1)	20(1)	26(1)	-3(1)	1(1)	-2(1)
N(11)	13(1)	17(1)	23(1)	1(1)	-1(1)	0(1)
N(12)	16(1)	23(1)	40(1)	4(1)	-3(1)	-4(1)
C(11)	13(1)	29(1)	49(2)	3(1)	-6(1)	-2(1)
C(12)	20(1)	25(1)	40(1)	3(1)	-5(1)	6(1)
C(13)	24(1)	19(1)	46(2)	9(1)	-1(1)	0(1)
C(14)	16(1)	21(1)	42(1)	7(1)	-1(1)	-3(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$)

	x	y	z	U(eq)
H(1)	10523	6411	2490	35
H(2)	9258	5424	889	35
H(3)	7334	4582	1967	34
H(4)	6816	4793	4587	27
H(11)	2017	7077	5733	37
H(12)	2744	8369	5208	35
H(13)	5602	8703	5390	36
H(14)	7544	7715	6199	32

Table 3. Crystal data and structure refinement for form III

Identification code	gb379	
Empirical formula	$C_8H_8Cl_2N_4Zn$	
Formula weight	296.45	
Temperature	220(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 25.4704(13) Å	α= 90°.
	b = 7.5932(4) Å	β= 90°.
	c = 11.7460(9) Å	γ = 90°.
Volume	2271.7(2) $Å^3$	
Z	8	
Density (calculated)	1.734 Mg/m^3	
Absorption coefficient	2.603 mm^{-1}	
F(000)	1184	
Crystal size	0.06 x 0.10 x 0.14 mm^3	
Theta range for data collection	2.36 to 26.92°.	
Index ranges	-30<=h<=30, -9<=k<=9, -14<=l<=14	
Reflections collected	15632	
Independent reflections	4685 [R(int) = 0.0333]	
Completeness to theta = 26.92°	96.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4685 / 1 / 272	
Goodness-of-fit on F^2	0.968	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0615	
R indices (all data)	R1 = 0.0311, wR2 = 0.0638	
Absolute structure parameter	0.060(10)	
Extinction coefficient	0.0011(3)	
Largest diff. peak and hole	0.332 and -0.461 e.$Å^{-3}$	

Remarks:

All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined isotropic (U_{eq}= -1.2) using a riding model with C-H = 0.95 Å for aromatic hydrogen atoms. There are two crystallographically independent molecules into the asymmetric unit, located at general positions.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2x10^3$) U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	-800(1)	2485(1)	2489(1)	20(1)
Cl(1)	-1247(1)	4995(1)	2656(1)	28(1)
Cl(2)	-1232(1)	-43(1)	2636(1)	29(1)
N(1)	-367(1)	2582(3)	1020(2)	23(1)
N(2)	-654(1)	2104(4)	100(2)	32(1)
C(1)	-418(2)	2151(5)	-902(3)	36(1)
C(2)	98(2)	2682(4)	-1068(3)	34(1)
C(3)	379(1)	3164(5)	-134(3)	28(1)
C(4)	126(1)	3102(4)	917(2)	24(1)
N(11)	-284(1)	2402(3)	3836(3)	23(1)
N(12)	188(1)	3120(4)	3641(2)	30(1)
C(11)	538(1)	3123(5)	4480(3)	33(1)
C(12)	431(2)	2440(4)	5562(3)	35(1)
C(13)	-50(1)	1749(4)	5746(3)	35(1)
C(14)	-408(2)	1761(5)	4844(3)	30(1)
Zn(2)	1676(1)	2926(1)	2037(1)	21(1)
Cl(3)	1215(1)	446(1)	1924(1)	33(1)
Cl(4)	1256(1)	5476(1)	1899(1)	30(1)
N(21)	2190(1)	2814(3)	678(2)	23(1)
N(22)	2665(1)	3473(4)	889(2)	32(1)
C(21)	3014(1)	3473(5)	47(3)	36(1)
C(22)	2906(2)	2852(4)	-1029(3)	35(1)
C(23)	2417(2)	2195(4)	-1241(3)	36(1)
C(24)	2061(2)	2213(4)	-344(3)	30(1)
N(31)	2131(1)	2844(3)	3478(2)	24(1)
N(32)	1857(1)	3284(4)	4418(2)	34(1)
C(31)	2111(2)	3271(5)	5404(3)	39(1)
C(32)	2632(2)	2827(5)	5525(3)	35(1)
C(33)	2905(1)	2357(4)	4575(3)	32(1)
C(34)	2631(1)	2408(4)	3552(3)	28(1)

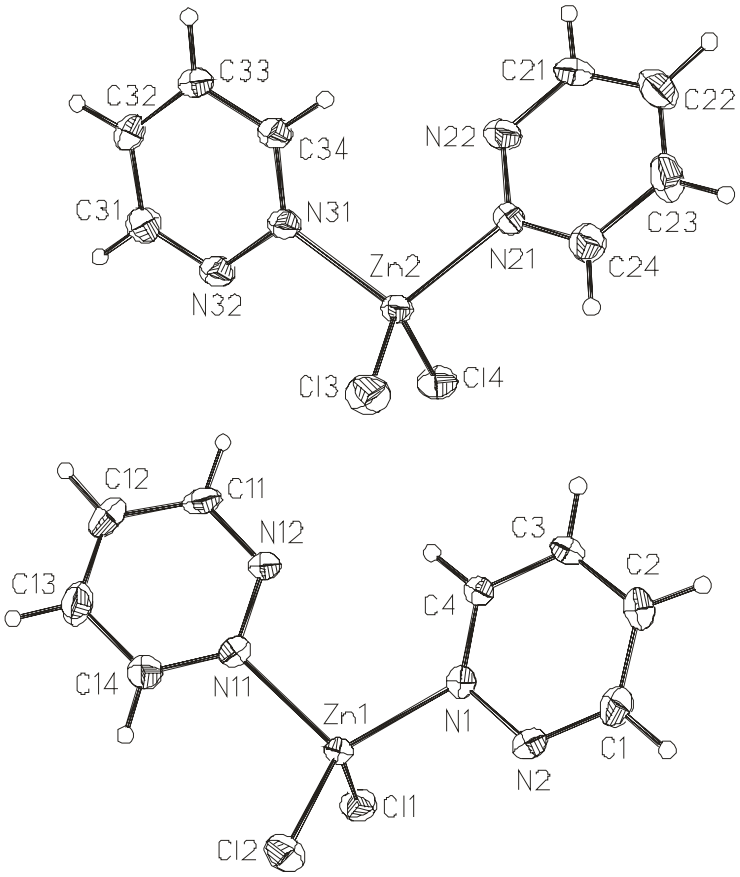

Table 3. Bond lengths [Å] and angles [°]

Zn(1)-N(1)	2.049(3)	Zn(2)-N(31)	2.053(3)
Zn(1)-N(11)	2.058(3)	Zn(2)-N(21)	2.065(3)
Zn(1)-Cl(2)	2.2188(7)	Zn(2)-Cl(4)	2.2181(7)
Zn(1)-Cl(1)	2.2282(7)	Zn(2)-Cl(3)	2.2236(7)
N(1)-Zn(1)-N(11)	107.71(11)	N(31)-Zn(2)-N(21)	106.20(10)
N(1)-Zn(1)-Cl(2)	111.31(7)	N(31)-Zn(2)-Cl(4)	111.02(7)
N(11)-Zn(1)-Cl(2)	103.33(7)	N(21)-Zn(2)-Cl(4)	106.58(7)
N(1)-Zn(1)-Cl(1)	108.56(7)	N(31)-Zn(2)-Cl(3)	108.76(8)
N(11)-Zn(1)-Cl(1)	106.55(7)	N(21)-Zn(2)-Cl(3)	104.70(8)
Cl(2)-Zn(1)-Cl(1)	118.68(3)	Cl(4)-Zn(2)-Cl(3)	118.69(3)
C(4)-N(1)-Zn(1)	126.8(2)	C(24)-N(21)-Zn(2)	123.9(3)
N(2)-N(1)-Zn(1)	111.9(2)	N(22)-N(21)-Zn(2)	114.6(2)
C(14)-N(11)-Zn(1)	123.2(3)	C(34)-N(31)-Zn(2)	127.4(2)
N(12)-N(11)-Zn(1)	115.5(2)	N(32)-N(31)-Zn(2)	112.1(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2 a^{*2} U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	15(1)	27(1)	18(1)	3(1)	0(1)	-1(1)
Cl(1)	24(1)	28(1)	33(1)	4(1)	-1(1)	3(1)
Cl(2)	28(1)	27(1)	33(1)	1(1)	4(1)	-6(1)
N(1)	22(2)	31(1)	17(1)	2(1)	0(1)	-1(1)
N(2)	21(2)	51(2)	23(1)	-1(1)	-4(1)	-6(1)
C(1)	36(2)	54(2)	19(2)	-5(1)	-4(1)	-12(2)
C(2)	35(2)	49(2)	19(2)	1(1)	4(2)	-1(1)
C(3)	17(2)	40(2)	26(2)	6(1)	4(1)	-5(1)
C(4)	18(2)	37(2)	18(2)	0(1)	1(1)	-3(1)
N(11)	20(2)	27(1)	23(2)	2(1)	-4(1)	1(1)
N(12)	17(1)	50(2)	22(1)	3(1)	-1(1)	-4(1)
C(11)	16(2)	53(2)	31(2)	-3(1)	-5(1)	-3(1)
C(12)	37(2)	41(2)	27(2)	-1(1)	-15(2)	4(1)
C(13)	44(2)	41(2)	21(2)	4(1)	-6(1)	-8(2)
C(14)	28(2)	37(2)	26(2)	1(1)	-1(1)	-7(1)
Zn(2)	16(1)	26(1)	20(1)	-2(1)	0(1)	-2(1)
Cl(3)	30(1)	27(1)	40(1)	1(1)	-3(1)	-9(1)
Cl(4)	26(1)	25(1)	38(1)	-1(1)	-1(1)	2(1)
N(21)	20(2)	29(2)	19(1)	0(1)	2(1)	-2(1)
N(22)	19(2)	50(2)	28(1)	-2(1)	1(1)	-6(1)
C(21)	15(2)	56(2)	36(2)	6(2)	3(1)	-1(1)
C(22)	33(2)	40(2)	33(2)	5(1)	13(2)	6(1)
C(23)	44(2)	42(2)	21(2)	-4(1)	7(1)	-4(2)
C(24)	29(2)	37(2)	24(2)	-4(1)	1(1)	-5(1)
N(31)	18(2)	31(2)	22(2)	-3(1)	1(1)	2(1)
N(32)	21(2)	56(2)	25(1)	-3(1)	3(1)	6(1)
C(31)	30(2)	66(2)	21(2)	-4(2)	5(1)	10(2)
C(32)	29(2)	56(2)	18(2)	3(1)	-7(1)	-1(2)
C(33)	18(2)	51(2)	27(2)	4(1)	-1(1)	3(1)
C(34)	20(2)	39(2)	24(2)	-1(1)	2(1)	6(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^{\ 3}$)

	x	y	z	U(eq)
H(3)	-612	1802	-1544	44
H(2)	248	2708	-1799	41
H(1)	731	3525	-195	33
H(4)	311	3441	1573	29
H(11)	872	3604	4341	40
H(12)	685	2463	6142	42
H(13)	-141	1274	6458	42
H(14)	-747	1300	4959	36
H(21)	3352	3921	193	43
H(22)	3163	2880	-1603	42
H(23)	2325	1750	-1960	43
H(24)	1719	1786	-465	36
H(31)	1922	3583	6062	47
H(32)	2794	2848	6243	41
H(33)	3260	2017	4609	38
H(34)	2811	2117	2879	33

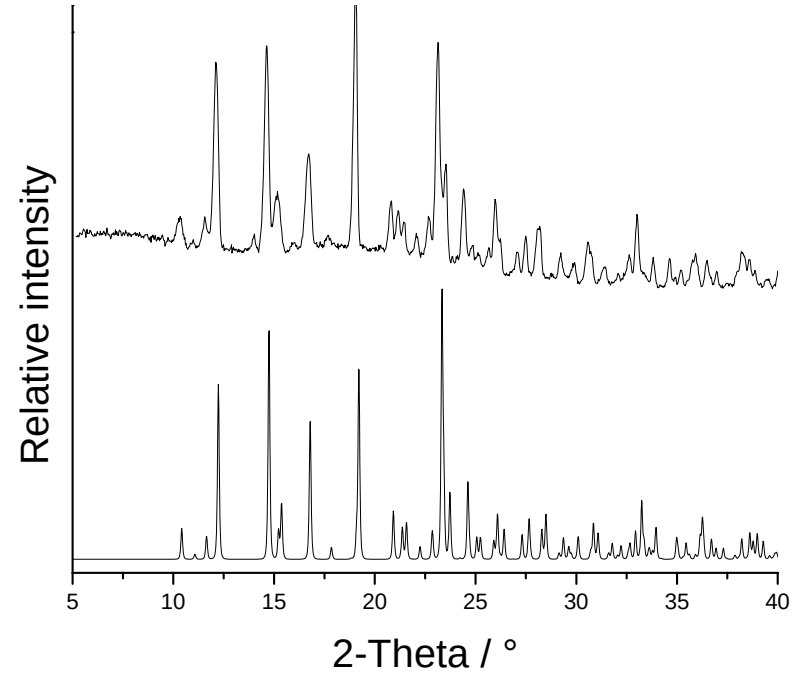

Fig. 1: Experimental X-ray powder pattern of form **I** (top) and theoretical pattern calculated from single crystal data (bottom).

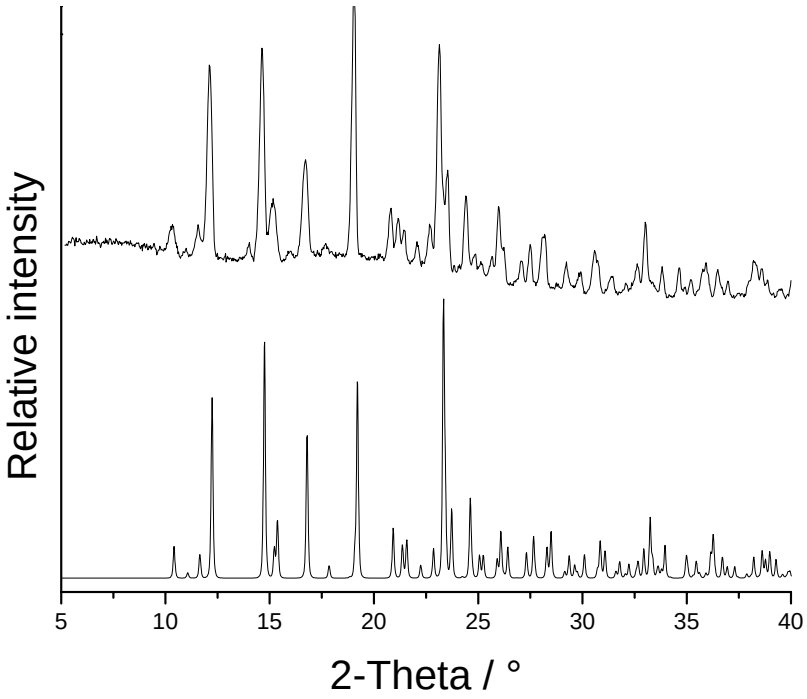

Fig. 2: Experimental X-ray powder pattern of form **II** (top) and theoretical pattern calculated from single crystal data (bottom).

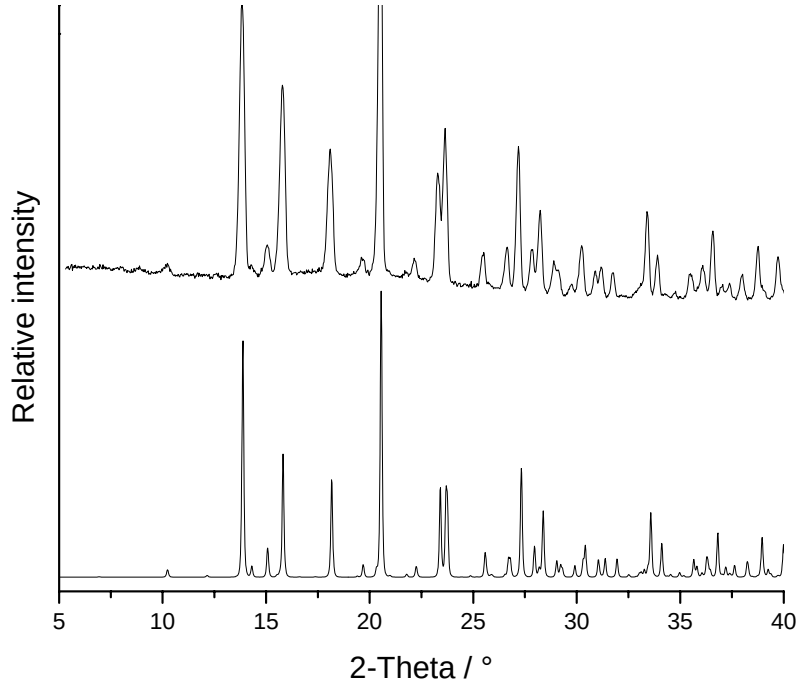

Fig. 3: Experimental X-ray powder pattern of form **III** (top) and theoretical pattern calculated from single crystal data (bottom).

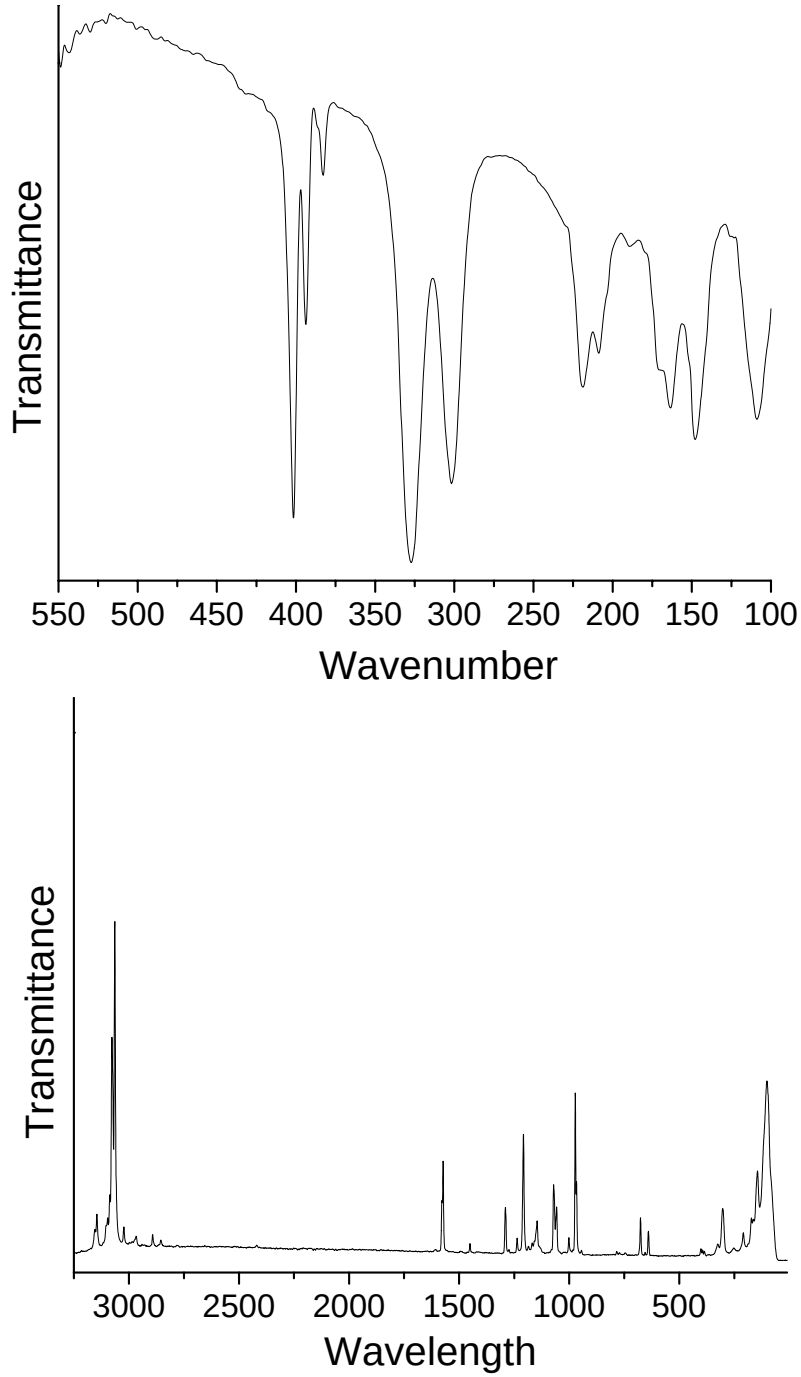

Figure 4:IR (top) and Raman (bottom) spectra for form **I**

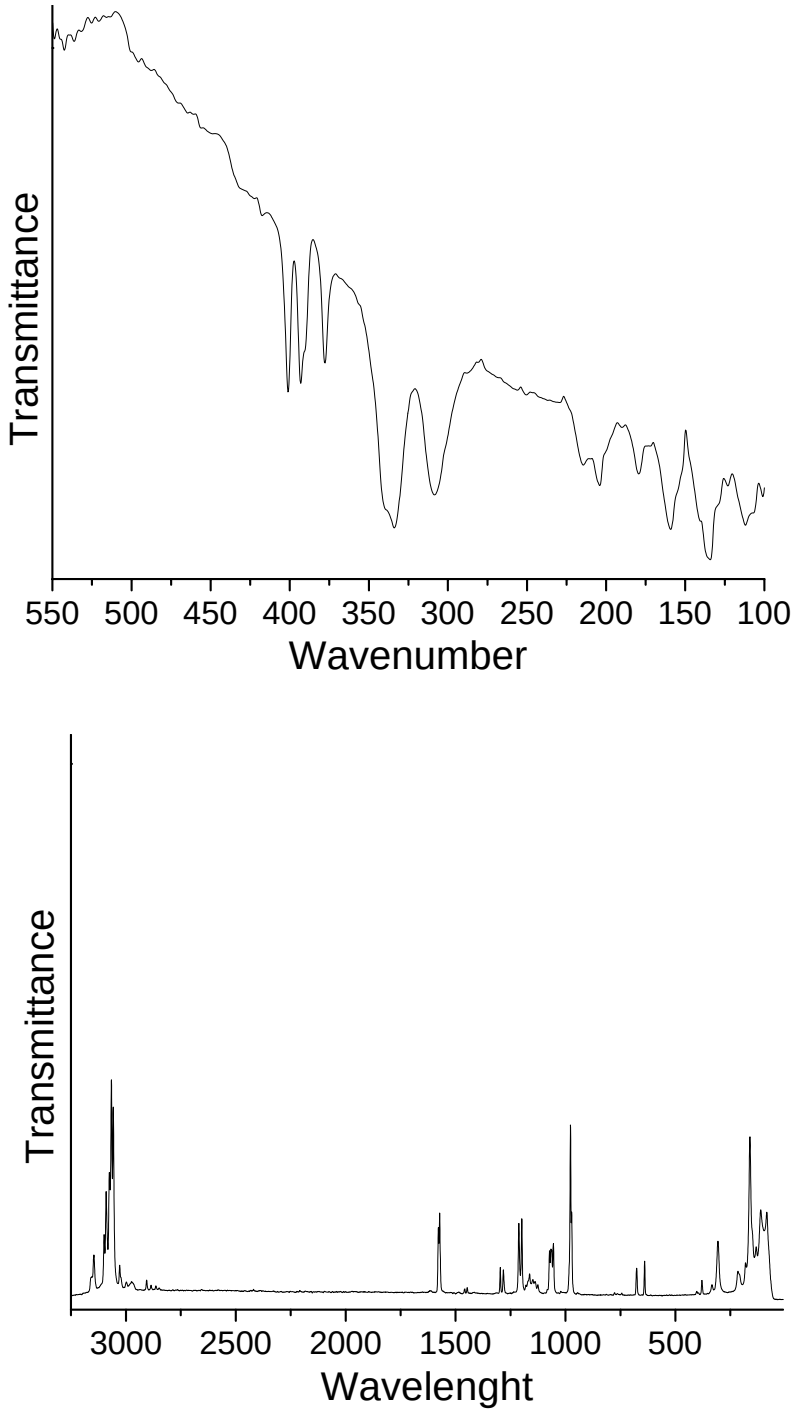

Figure 5: IR (top) and Raman (bottom) spectra for form **II**

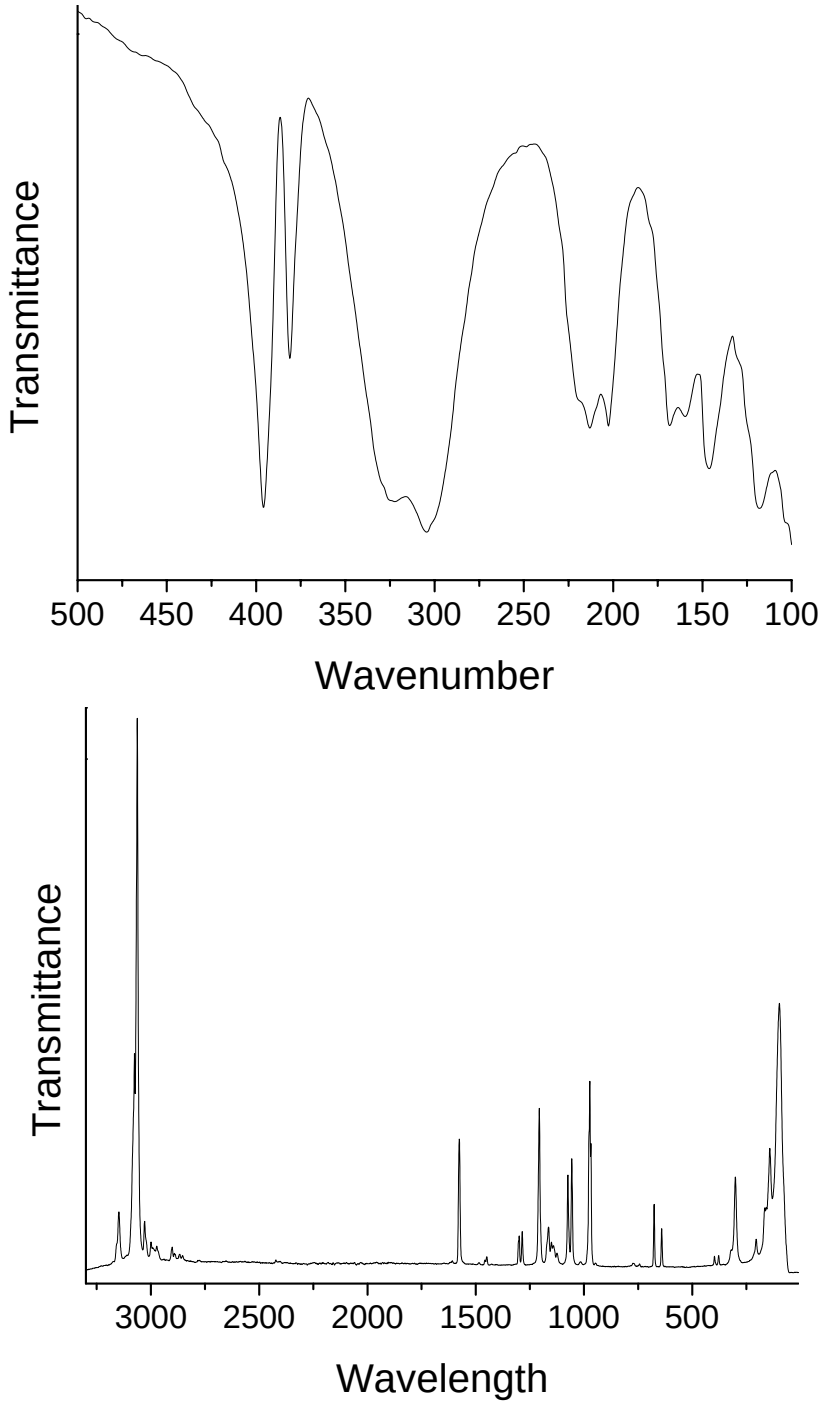

Figure 6: IR (top) and Raman (bottom) spectra for form **III**