Electronic Supplementary Information for Dalton Transactions

Supporting Information (S) for Paper:

Alkali and transition metal (Ag, Cu) salts of bridged 5-nitrotetrazole derivatives for energetic applications

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Table S1. Calculated (corrected) and experimental frequencies with the corresponding intensities (IR) and activities (Raman) and tentative assignment for the $NTTz^-$ anion.

	ν_{calc} (cm^{-1}) [a]	ν_{meas} (cm^{-1}) [b] (IR / Raman)	IR intensity [c] (Calc / Obs)	Raman activity [d] (Calc / Obs)	Mode Assignment [e]
1	62	- / 90(3)	3.2 / -	0.6 / w	$\tau(NO_2) + \tau$(NT-ring)
2	320	- / 310(5)	1.9 / -	2.3 / w	$\tau(CH_2)$
3	351	- / 346(5)	0.9 / -	1.4 / w	$\tau(CH_2)$
4	530	548(6) / 548(8)	2.2 / w	4.2 / m	$\omega(NO_2)$
5	646	656(2) / n.o.	17.2 / m	2.3 / n.o.	$\gamma(NO_2) + \gamma$(NT-ring) + γ(Tz-ring)
6	669	684(1) / 686(4)	6.9 / w	4.4 / m	$\gamma(NO_2) + \gamma$(NT-ring) + γ(Tz-ring)
7	696	705(2) / n.o.	2.0 / w	0.3 / n.o.	γ(NT-ring) + γ(Tz-ring)
8	722	n.o. / n.o.	37.0 / n.o.	2.4 / n.o.	γ(N6–N7–N8)
9	727	752(1) / n.o.	30.1 / m	0.6 / n.o.	γ(N6–N7–N8)
10	765	759(1) / 759(6)	1.6 / w	2.5 / m	$\gamma(NO_2) + \gamma$(NT-ring)
11	795	785(1) / 774(1)	8.1 / w	0.6 / w	$\omega(CH_2)$
12	825	846(3) / 844(1)	92.5 / s	1.8 / w	$\delta(NO_2)$
13	1020	1031(3) / n.o.	3.9 / w	4.3 / n.o.	δ(C3–N9–N8)$_{Tz\text{-}ring}$
14	1042	1048(8) / 1032(3)	5.6 / w	47.9 / s	δ(N6–C3–N9)$_{Tz\text{-}ring}$
15	1048	1070(2) / 1070(2)	4.6 / w	14.1 / m	δ(N4–N5–C1)$_{NT\text{-}ring}$
16	1086	1101(3) / 1099(2)	2.1 / w	41.2 / m	ν_{as}(N–N)$_{NT\text{-}ring}$ + $\omega(CH_2)$
17	1133	1125(9) / 1105(1)	8.6 / w	5.7 / m	ν(N6–N7)$_{Tz\text{-}ring}$ + ν(N8–N9)$_{Tz\text{-}ring}$
18	1163	1145(1) / 1145(3)	9.6 / w	3.6 / m	ν(N7–N8)$_{Tz\text{-}ring}$ + $\gamma_{sym}(CH_2)$
19	1220	1219(1) / 1195(3)	10.7 / w	49.1 / s	$\omega(CH_2) + \nu$(N4–N5)
20	1268	n.o. / n.o.	37.3 / n.o.	8.2 / n.o.	$\gamma_{as}(CH_2)$
21	1279	1278(1) / 1280(1)	28.6 / m	8.5 / m	$\gamma(CH_2)$
22	1313	1297(1) / 1298(1)	3.1 / w	26.9 / w	ν(C1–N2) + ν(N2–N3)
23	1316	1325(5) / 1320(3)	106.0 / s	7.0 / m	ν(C1–N5) + $\nu_{sym}(NO_2)$
24	1374	1342(6) / 1341(7)	39.7 / m	33.9 / m	$\delta(CH_2)$
25	1400	1419(2) / 1421(2)	24.9 / s	2.1 / w	ν(C3–N)$_{Tz\text{-}ring}$
26	1415	1437(3) / 1445(2)	1.2 / m	26.7 / s	ν(C2–C3)$_{Tz\text{-}ring}$
27	1451	1488(2) / 1489(2)	22.7 / s	58.5 / m	ν(C–N)$_{NT\text{-}ring}$ + ν(N–N)$_{NT\text{-}ring}$
28	1590	1558(3) / 1560(4)	220.1 / s	7.1 / m	$\nu_{as}(NO_2)$
29	2961	n.o. / 2974(5)	20.0 / n.o.	132.0 / m	$\nu_{sym}(CH_2)$
30	3026	3022(8) / 3024(5)	2.6 / m	60.9 / m	$\nu_{as}(CH_2)$

[a] Calculated frequencies scaled by 0.9613. [b] Averaged values of measured (IR and Raman) frequencies with standard deviations in curved brackets (n.o. = not observed). [c] Calculated intensities and observed intensities (IR). [d] Calculated and observed activities (Raman). [e] Tentative assignement of the vibrational modes (ν = stretching, δ = in-plane bending, γ = out-of-plane bending, ω = in plane rocking, τ = torsion, as = asymmetric and sym = symmetric).

Table S2. Selected bond lengths [Å] and angles [°] for **8** and **9**.

Parameter	**8 (A)**	**8 (B)**	**9 (A)**	**9 (B)**
N1–O1	1.224(1)	1.218(1)	1.221(3)	1.226(3)
N1–O2	1.221(1)	1.221(1)	1.221(3)	1.220(2)
N1–C1	1.447(1)	1.450(1)	1.444(3)	1.440(3)
N2–C1	1.319(1)	1.319(1)	1.308(3)	1.319(3)
N2–N3	1.320(1)	1.317(1)	1.322(2)	1.321(2)
N3–N4	1.326(1)	1.327(1)	1.321(2)	1.325(2)
N4–N5	1.320(1)	1.320(1)	1.326(3)	1.324(3)
N5–C1	1.334(1)	1.329(1)	1.331(3)	1.325(3)
N3–C2	1.473(1)	1.476(1)	1.475(3)	1.468(3)
C2–C3	1.490(1)	1.484(1)	1.485(3)	1.498(3)
C3–N6	1.328(1)	1.326(1)	1.322(3)	1.322(3)
N6–N7	1.353(1)	1.345(1)	1.347(3)	1.356(3)
N8–N7	1.304(1)	1.311(1)	1.317(3)	1.326(3)
N9–N8	1.348(1)	1.346(1)	1.345(3)	1.349(3)
N9–C3	1.326(1)	1.330(1)	1.319(3)	1.307(3)
O1–N1–O2	125.7(1)	125.9(1)	125.9(2)	125.6(2)
O1–N1–C1	117.2(1)	118.0(1)	117.4(2)	117.3(2)
O2–N1–C1	117.0(1)	115.9(1)	116.6(2)	117.1(2)
N2–C1–N1	121.2(1)	122.2(1)	123.2(2)	121.6(2)
C1–N2–N3	99.7(1)	99.7(1)	100.0(2)	99.9(2)
N2–N3–N4	114.3(1)	114.3(1)	114.3(2)	114.4(2)
N5–N4–N3	106.4(1)	106.1(1)	105.9(2)	105.8(2)
N4–N5–C1	104.1(1)	104.2(1)	104.3(2)	104.7(2)
N5–C1–N1	123.1(1)	122.2(1)	121.4(2)	123.2(2)
N2–N3–C2	122.8(1)	121.9(1)	122.3(2)	122.8(2)
N4–N3–C2	122.7(1)	123.6(1)	123.3(2)	122.6(2)
N3–C2–C3	111.1(1)	110.8(1)	110.8(2)	111.5(2)
N2–C1–N5	115.5(1)	115.4(1)	115.4(2)	115.1(2)
N6–C3–C2	124.5(1)	123.4(1)	123.2(2)	123.8(2)
C3–N6–N7	104.3(1)	104.2(1)	104.0(2)	104.1(2)
N6–N7–N8	109.5(1)	109.7(1)	109.2(2)	109.3(2)
N7–N8–N9	109.2(1)	109.0(1)	109.3(2)	109.4(2)
C3–N9–N8	104.7(1)	104.7(1)	104.2(2)	104.3(2)
N6–C3–N9	112.1(1)	112.1(1)	113.2(2)	112.7(2)
N9–C3–C2	123.3(1)	124.3(1)	123.6(2)	123.5(2)

Table S3. Selected bond distances for the coordination around the K^+ cations in **8**.

K1–O5	2.783(1)	K1–O1	3.002(1)	K2–N16^{ii}	2.999(1)
K1–O4	2.799(1)	K2–O6	2.744(1)	K2–N4	3.089(1)
K1–O5^{iv}	2.819(1)	K2–N17	2.765(1)	K2–N16	3.130(1)
K1–N2	2.868(1)	K2–O6^{i}	2.874(1)	K2–N5^{ii}	3.172(1)
K1–N14	2.965(1)	K2–N18	2.897(1)		

Symmetry codes for **8**: (i) 2–x, 1–y, –z; (ii) 2–x, 2–y, –z; (iii) 1–x, 2–y, –z; (iv) 3–x, 2–y, –1–z; (v) 3–x, 1–y, –1–z.

Table S4. Selected bond angles for the coordination around the K^+ cations in **8**.

O5–K1–O4	103.68(3)	N6–K1–O3^{v}	74.45(3)	O6–K2–N5^{ii}	72.86(3)
O5–K1–O5^{iv}	83.99(3)	O5–K1–N10^{v}	85.95(3)	N17–K2–N5^{ii}	69.68(3)
O4–K1–O5^{iv}	85.23(4)	N2–K1–N10^{v}	140.76(3)	O6^{i}–K2–N5^{ii}	137.00(3)
O5–K1–N2	104.56(3)	N14–K1–N10^{v}	116.38(3)	N18–K2–N5^{ii}	141.92(3)
O4–K1–N2	138.61(3)	O1–K1–N10^{v}	164.03(3)	N16^{ii}–K2–N5^{ii}	75.44(3)
O5^{iv}–K1–N2	127.26(3)	N6–K1–N10^{v}	74.41(3)	N4–K2–N5^{ii}	119.73(3)
O5–K1–N14	150.92(3)	O3^{v}–K1–N10^{v}	20.51(3)	N16–K2–N5^{ii}	59.70(3)
O4–K1–N14	97.07(3)	O4–K1–N10^{v}	19.36(3)	O6–K2–N17^{iii}	103.81(3)
O5^{iv}–K1–N14	77.61(3)	O5^{iv}–K1–N10^{v}	90.97(3)	N17–K2–N17^{iii}	67.46(3)
N2–K1–N14	70.65(3)	O6–K2–N17	127.66(3)	O6^{i}–K2–N17^{iii}	97.06(3)
O5–K1–O1	84.43(3)	O6–K2–O6^{i}	78.34(3)	N18–K2–N17^{iii}	22.58(3)
O4–K1–O1	158.18(4)	N17–K2–O6^{i}	151.33(3)	N16^{ii}–K2–N17^{iii}	161.56(3)
O5^{iv}–K1–O1	75.39(3)	O6–K2–N18	102.10(3)	N4–K2–N17^{iii}	92.95(3)
N2–K1–O1	54.56(2)	N17–K2–N18	86.62(3)	N16–K2–N17^{iii}	91.05(3)
N14–K1–O1	69.33(3)	O6^{i}–K2–N18	74.74(3)	N5^{ii}–K2–N17^{iii}	120.22(3)
O5–K1–N6	122.45(3)	O6–K2–N16^{ii}	89.74(3)	O6–K2–N15^{ii}	81.86(3)
O4–K1–N6	71.40(3)	N17–K2–N16^{ii}	113.97(3)	N17–K2–N15^{ii}	134.89(3)
O5^{iv}–K1–N6	147.67(3)	O6^{i}–K2–N16^{ii}	73.16(3)	O6^{i}–K2–N15^{ii}	50.59(3)
N2–K1–N6	68.04(3)	N18–K2–N16^{ii}	142.60(3)	N18–K2–N15^{ii}	123.53(3)
N14–K1–N6	83.31(3)	O6–K2–N4	149.91(3)	N16^{ii}–K2–N15^{ii}	22.88(3)
O1–K1–N6	121.55(3)	N17–K2–N4	81.75(3)	N4–K2–N15^{ii}	70.63(3)
O5–K1–O3^{v}	70.04(3)	O6^{i}–K2–N4	74.89(3)	N16–K2–N15^{ii}	110.62(3)
O4–K1–O3^{v}	39.53(3)	N18–K2–N4	83.94(3)	N5^{ii}–K2–N15^{ii}	93.64(3)
O5^{iv}–K1–O3^{v}	101.62(3)	N16^{ii}–K2–N4	69.61(3)	N17^{iii}–K2–N15^{ii}	145.99(3)
N2–K1–O3^{v}	130.53(3)	O6–K2–N16	131.14(3)		
N14–K1–O3^{v}	135.53(3)	N17–K2–N16	24.73(3)	N4–K2–N16	72.16(3)
O1–K1–O3^{v}	154.47(3)	O6^{i}–K2–N16	146.40(3)	N18–K2–N16	107.76(3)

Symmetry codes for **8**: (i) 2-x, 1-y, -z; (ii) 2-x, 2-y, -z; (iii) 1-x, 2-y, -z; (iv) 3-x, 2-y, -1-z; (v) 3-x, 1-y, -1-z.

Table S5. Hydrogen bonding geometry in **8** and **9**.

D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (º)
		8		
O6–H6•••N6^{i}	0.83(2)	1.93(2)	2.743(1)	166(2)
O6–H5•••N9^{ii}	0.85(2)	2.04(2)	2.878(1)	168(2)
O5–H7•••N6^{iii}	0.80(2)	2.22(2)	3.010(1)	172(2)
O5–H8•••N7^{iv}	0.77(2)	2.19(2)	2.949(1)	169(2)
C2–H1•••O1^{v}	0.99(1)	2.40(1)	3.205(1)	138(1)
C5–H5•••N16^{vi}	0.96(2)	2.73(2)	3.221(1)	112(1)
		9		
O5–H7•••N15^{i}	0.76(3)	2.24(3)	3.006(3)	178(3)
O5–H8•••N16^{ii}	0.80(4)	2.15(4)	2.946(3)	166(4)
O6–H5•••N18^{iii}	0.83(4)	2.03(4)	2.835(3)	161(3)
O6–H6•••N6^{iii}	0.81(3)	1.99(3)	2.777(4)	164(3)
C5–H4•••O3^{iv}	0.95(2)	2.40(2)	3.197(3)	141(2)

Symmetry codes for **8**: (i) x, –1+y, z; (ii) 2–x, 1–y, –z; (iii) 2–x, 2–y, –1–z; (iv) –1+x, 2+y, 1+z; (v) –2+x, 1+y, 1+z; (vi) 1–x, 3–y, –z. **9**: (i) –1–x, 2–y, 1–z; (ii) –1+x, y, z; (iii) –x, 2–y, –z; (iv) x, y+1, z.

Table S6. Graph-set matrix for selected hydrogen bonds in **8**. First level motifs on-diagonal and second level graph-sets off-diagonal.

D–H•••A	O5–H7•••N6^{iii}	O5–H8•••N7^{iv}	O6–H5•••N9^{ii}	O6–H6•••N6^{i}
O5–H7•••N6^{iii}	D1,1(2)			
O5–H8•••N7^{iv}	R4,4(10)	D1,1(2)		
O6–H5•••N9^{ii}	D2,2(5)	D2,2(5)	D1,1(2)	
O6–H6•••N6^{i}	D2,2(5)	D2,2(5)	D2,2(5)	D1,1(2)

Symmetry codes for **8**: (i) x, -1+y, z; (ii) 2-x, 1-y, -z; (iii) 2-x, 2-y, -1-z; (iv) -1+x, 2+y, 1+z.

Table S7. Graph-set matrix for selected hydrogen bonds in **9**. First level motifs on-diagonal and second level graph-sets off-diagonal.

D–H•••A	O5–H7•••N15^{i}	O5–H8•••N16^{ii}	O6–H5•••N18^{iii}	O6–H6•••N6^{iii}
O5–H7•••N15^{i}	D1,1(2)			
O5–H8•••N16^{ii}	R4,4(10)	D1,1(2)		
O6–H5•••N18^{iii}	D2,2(5)	D2,2(5)	D1,1(2)	
O6–H6•••N6^{iii}	D2,2(5)	D2,2(5)	D2,2(5)	D1,1(2)

Symmetry codes for **9**: (i) -1-x, 2-y, 1-z; (ii) -1+x, y, z; (iii) –x, 2-y, -z.

Table S8. Selected bond distances for the coordination around the Rb^{+} cations in **9**.

Rb1–O5	2.912(2)	Rb1–O2	3.528(2)	Rb2–N7	3.110(2)
Rb1–O2^{iv}	2.941(2)	Rb1–N1^{iv}	3.569(2)	Rb2–N13	3.185(2)
Rb1–O5^{v}	2.977(2)	Rb1–O1^{vi}	3.627(2)	Rb2–N14^{i}	3.299(2)
Rb1–N11	2.998(2)	Rb2–N8^{i}	2.899(2)	Rb2–N7^{i}	3.327(2)
Rb1–N5	3.119(2)	Rb2–O6	2.930(2)	Rb2–N8^{ii}	3.416(2)
Rb1–O3	3.161(2)	Rb2–N9^{ii}	2.994(2)	Rb2–N6^{iii}	3.580(2)
Rb1–N15	3.349(2)	Rb2–O6^{iii}	3.002(2)	Rb2–N6	3.592(2)
Rb1–O1^{iv}	3.505(2)				

Symmetry codes for **9**: (i) –1–x, 2–y, –z; (ii) x, 1+y, z; (iii) –x, 2–y, –z; (iv) –x, 1–y, 1–z; (v) –1–x, 1–y, 1–z; (vi) –1+x, 1+y, z; (vii) 1+x, –1+y, z.

Table S9. Selected bond angles for the coordination around the Rb^+ cations in **9**.

O2–Rb1–O1^{vi}	144.56(5)	N11–Rb1–N1^{iv}	145.01(5)	N14^{i}–Rb2–N7^{i}	58.82(5)
N1^{iv}–Rb1–O1^{vi}	90.47(6)	N5–Rb1–N1^{iv}	118.55(6)	N8^{i}–Rb2–N8^{ii}	72.11(6)
O5–Rb1–O2^{iv}	98.20(7)	O3–Rb1–N1^{iv}	162.97(5)	O6–Rb2–N8^{ii}	110.32(6)
O5–Rb1–O5^{v}	84.33(6)	N15–Rb1–N1^{iv}	79.29(5)	N9^{ii}–Rb2–N8^{ii}	23.04(5)
O2^{iv}–Rb1–O5^{v}	81.35(7)	O1^{iv}–Rb1–N1^{iv}	19.85(5)	O6^{iii}–Rb2–N8^{ii}	93.27(5)
O5–Rb1–N11	109.20(6)	O2–Rb1–N1^{iv}	72.89(6)	N7–Rb2–N8^{ii}	157.53(5)
O2^{iv}–Rb1–N11	142.05(6)	O5–Rb1–O1^{vi}	66.55(5)	N13–Rb2–N8^{ii}	89.65(5)
O5^{v}–Rb1–N11	126.04(6)	O2^{iv}–Rb1–O1^{vi}	104.35(6)	N14^{i}–Rb2–N8^{ii}	125.50(5)
O5–Rb1–N5	151.15(6)	O5^{v}–Rb1–O1^{vi}	150.78(5)	N7^{i}–Rb2–N8^{ii}	93.19(5)
O2^{iv}–Rb1–N5	99.96(6)	N11–Rb1–O1^{vi}	65.66(5)	N8^{i}–Rb2–N6^{iii}	118.11(6)
O5^{v}–Rb1–N5	76.50(6)	N5–Rb1–O1^{vi}	128.95(5)	O6–Rb2–N6^{iii}	49.26(5)
N11–Rb1–N5	67.52(5)	O3–Rb1–O1^{vi}	98.96(4)	N9^{ii}–Rb2–N6^{iii}	60.93(5)
O5–Rb1–O3	89.44(6)	N15–Rb1–O1^{vi}	61.01(5)	O6^{iii}–Rb2–N6^{iii}	77.56(5)
O2^{iv}–Rb1–O3	156.63(6)	O1^{iv}–Rb1–O1^{vi}	73.01(5)	N7–Rb2–N6^{iii}	123.45(5)
O5^{v}–Rb1–O3	77.44(6)	N8^{i}–Rb2–O6	125.38(6)	N13–Rb2–N6^{iii}	133.47(5)
N11–Rb1–O3	51.79(5)	N8^{i}–Rb2–N9^{ii}	91.32(6)	N14^{i}–Rb2–N6^{iii}	107.07(5)
N5–Rb1–O3	65.65(5)	O6–Rb2–N9^{ii}	109.74(6)	N7^{i}–Rb2–N6^{iii}	139.48(5)
O5–Rb1–N15	123.37(5)	N8^{i}–Rb2–O6^{iii}	146.89(6)	N8^{ii}–Rb2–N6^{iii}	63.00(5)
O2^{iv}–Rb1–N15	76.19(6)	O6–Rb2–O6^{iii}	87.34(6)	N8^{i}–Rb2–N6	134.63(6)
O5^{v}–Rb1–N15	146.23(5)	N9^{ii}–Rb2–O6^{iii}	70.30(6)	O6–Rb2–N6	78.23(5)
N11–Rb1–N15	66.97(5)	N8^{i}–Rb2–N7	114.54(6)	N9^{ii}–Rb2–N6	118.56(5)
N5–Rb1–N15	82.87(5)	O6–Rb2–N7	83.92(6)	O6^{iii}–Rb2–N6	48.80(5)
O3–Rb1–N15	117.68(5)	N9^{ii}–Rb2–N7	136.59(6)	N7–Rb2–N6	21.68(5)
O5–Rb1–O1^{iv}	66.05(6)	O6^{iii}–Rb2–N7	69.44(6)	N13–Rb2–N6	71.19(5)
O2^{iv}–Rb1–O1^{iv}	38.19(6)	N8^{i}–Rb2–N13	83.33(6)	N14^{i}–Rb2–N6	92.82(5)
O5^{v}–Rb1–O1^{iv}	98.13(6)	O6–Rb2–N13	148.38(5)	N7^{i}–Rb2–N6	111.67(5)
N11–Rb1–O1^{iv}	135.52(5)	N9^{ii}–Rb2–N13	79.12(5)	N8^{ii}–Rb2–N6	141.56(5)
N5–Rb1–O1^{iv}	137.42(5)	O6^{iii}–Rb2–N13	66.63(5)	N6^{iii}–Rb2–N6	106.51(4)
O3–Rb1–O1^{iv}	155.47(5)	N7–Rb2–N13	70.64(5)	N8^{i}–Rb2–O4^{i}	66.67(6)
N15–Rb1–O1^{iv}	79.36(5)	N8^{i}–Rb2–N14^{i}	67.56(5)	O6–Rb2–O4^{i}	59.56(5)
O5–Rb1–O2	137.32(6)	O6–Rb2–N14^{i}	69.08(6)	N9^{ii}–Rb2–O4^{i}	104.27(5)
O2^{iv}–Rb1–O2	54.57(7)	N9^{ii}–Rb2–N14^{i}	148.12(5)	O6^{iii}–Rb2–O4^{i}	143.26(5)
O5^{v}–Rb1–O2	61.51(6)	O6^{iii}–Rb2–N14^{i}	139.26(5)	N7–Rb2–O4^{i}	117.62(5)
N11–Rb1–O2	111.48(5)	N7–Rb2–N14^{i}	75.23(5)	N13–Rb2–O4^{i}	149.76(5)
N5–Rb1–O2	47.15(5)	N13–Rb2–N14^{i}	119.42(5)	N14^{i}–Rb2–O4^{i}	46.23(5)
O3–Rb1–O2	105.71(5)	N8^{i}–Rb2–N7^{i}	23.13(5)	N7^{i}–Rb2–O4^{i}	77.13(5)
N15–Rb1–O2	84.85(5)	O6–Rb2–N7^{i}	127.02(6)	N8^{ii}–Rb2–O4^{i}	84.84(5)
O1^{iv}–Rb1–O2	92.70(5)	N9^{ii}–Rb2–N7^{i}	109.29(5)	N6^{iii}–Rb2–O4^{i}	68.92(4)
O5–Rb1–N1^{iv}	81.30(6)	O6^{iii}–Rb2–N7^{i}	139.55(5)	N6–Rb2–O4^{i}	127.94(4)

Symmetry codes for **9**: (i) -1-x, 2-y, -z; (ii) x, 1+y, z; (iii) -x, 2-y, -z; (iv) -x, 1-y, 1-z; (v) -1-x, 1-y, 1-z; (vi) -1+x, 1+y, z; (vii) 1+x, -1+y, z.