Supporting Information for:

Synthesis, crystal structure, and magnetic properties of one-dimensional alkali metal copper chlor-tellurites $A(NH_4)Cu_4Te_2O_6Cl_6$ (A=K,Cs) , $NaCu_4Te_2Cl_5O_6$ and $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$

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Figure S1. Calculated and observed powder X-ray diffraction patterns for $Cs(NH_4)Cu_4Te_2Cl_6O_6$, $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$ and $K(NH_4)Cu_4Te_2Cl_6O_6$.
Figure S2.The corresponding EDX spectra for $Cs(NH_4)Cu_4Te_2Cl_6O_6$.
Figure S3.The corresponding EDX spectra for $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.
Figure S4.The corresponding EDX spectra for $K(NH_4)Cu_4Te_2Cl_6O_6$.
Figure S5.The corresponding EDX spectra for $NaCu_4Te_2Cl_5O_6$.
Figure S6. Infrared spectra of $Cs(NH_4)Cu_4Te_2Cl_6O_6$, $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$ and $K(NH_4)Cu_4Te_2Cl_6O_6$.
Figure S7. TGA diagram for $Cs(NH_4)Cu_4Te_2Cl_6O_6$.
Figure S8. TGA diagram for $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.
Figure S9. TGA diagram for $K(NH_4)Cu_4Te_2Cl_6O_6$.

Table S1: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Cs(NH_4)Cu_4Te_2Cl_6O_6$.
Table S2. Harmonic displacement parameters obtained for the compound $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Table S3. Bond lengths **(**Å) and Band angles (degrees) of $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Table S4. BVS of the atoms in $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Table S5: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Table S6. Harmonic displacement parameters obtained for the compound $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Table S7. Bond lengths **(**Å) and Band angles (degrees) of $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Table S8. BVS of the atoms in $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Table S9: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $K(NH_4)Cu_4Te_2Cl_6O_6$.

Table S10. Harmonic displacement parameters obtained for the compound $K(NH_4)Cu_4Te_2Cl_6O_6$.

Table S11. Bond lengths **(**Å) and Band angles (degrees) of $K(NH_4)Cu_4Te_2Cl_6O_6$.

Table S12. BVS of the atoms in $K(NH_4)Cu_4Te_2Cl_6O_6$.

Table S13: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $NaCu_4Te_2Cl_5O_6$.

Table S14. Harmonic displacement parameters obtained for the compound $NaCu_4Te_2\ Cl_5O_6$.

Table S15. Bond lengths **(**Å) and Band angles (degrees) of $NaCu_4Te_2\ Cl_5O_6$.

Table S16. BVS of the atoms in $NaCu_4Te_2Cl_5O_6$.

Table S17. Geometrical Parameters Associated with the M- O•••O -M Super-Supperexchange Paths of $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Table S18. Geometrical Parameters Associated with the M- O•••O - M Super-Supperexchange Paths of $K(NH_4)Cu_4Te_2Cl_6O_6$.

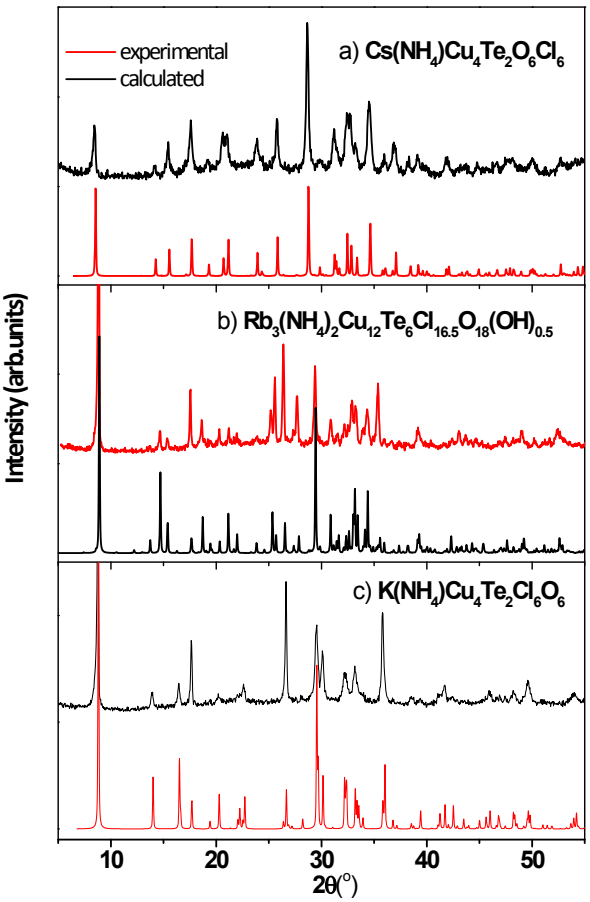


Figure S1. Calculated and observed powder X-ray diffraction patterns for $Cs(NH_4)Cu_4Te_2Cl_6O_6$, $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$ and $K(NH_4)Cu_4Te_2Cl_6O_6$.

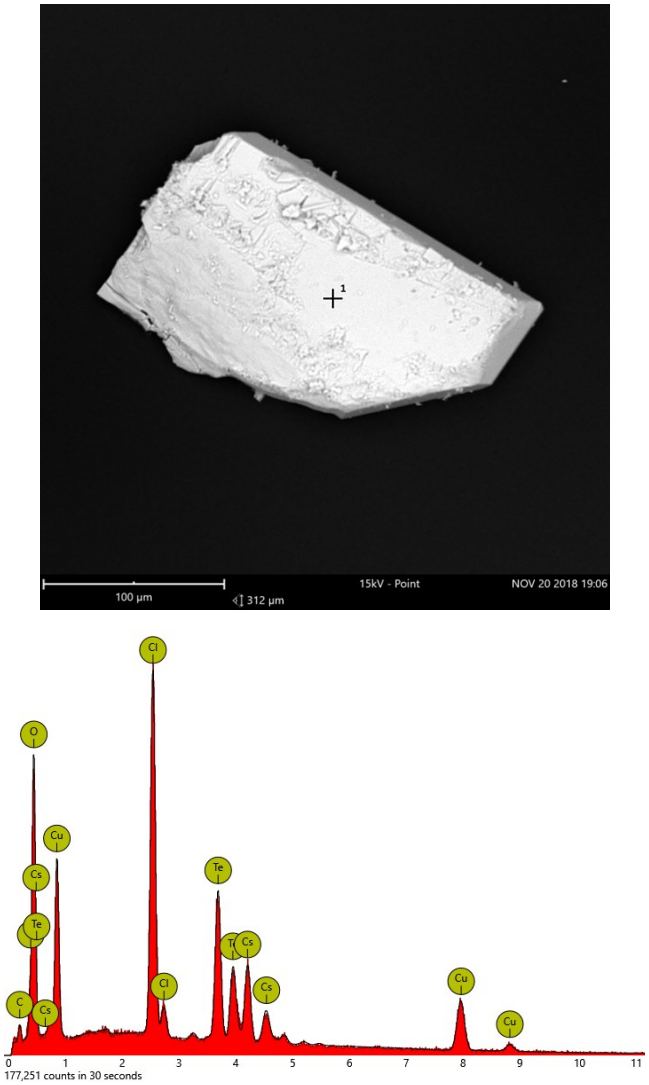


Figure S2**.**The corresponding EDX spectra for $Cs(NH_4)Cu_4Te_2O_6Cl_6$.

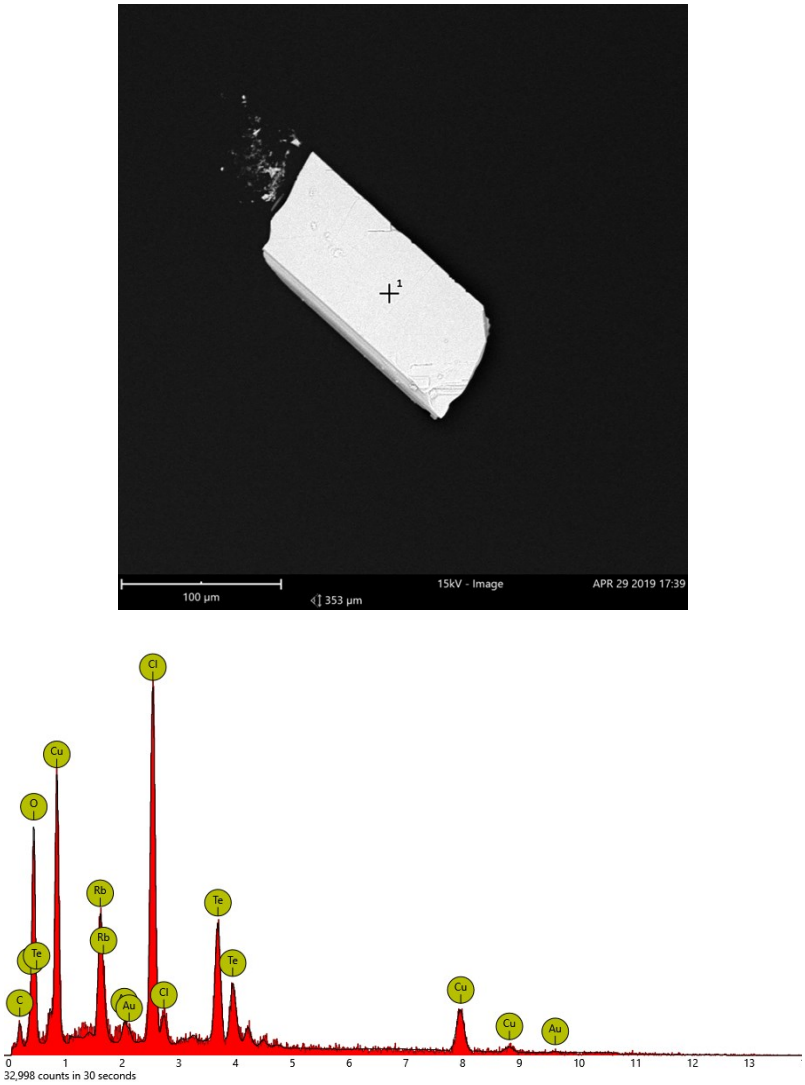
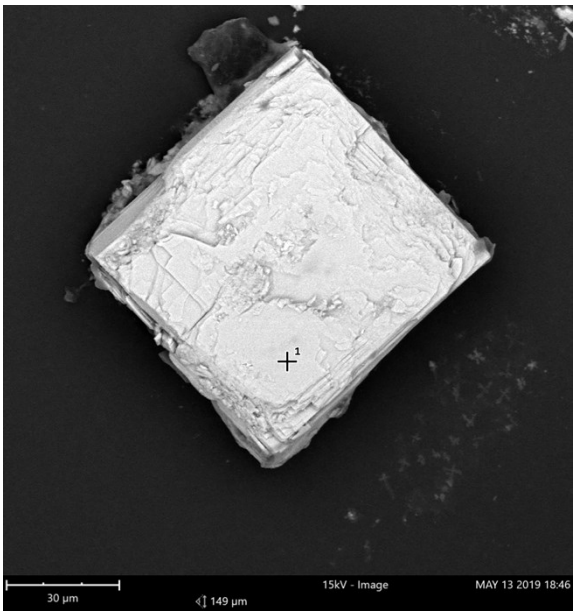


Figure S3. The corresponding EDX spectra for $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.



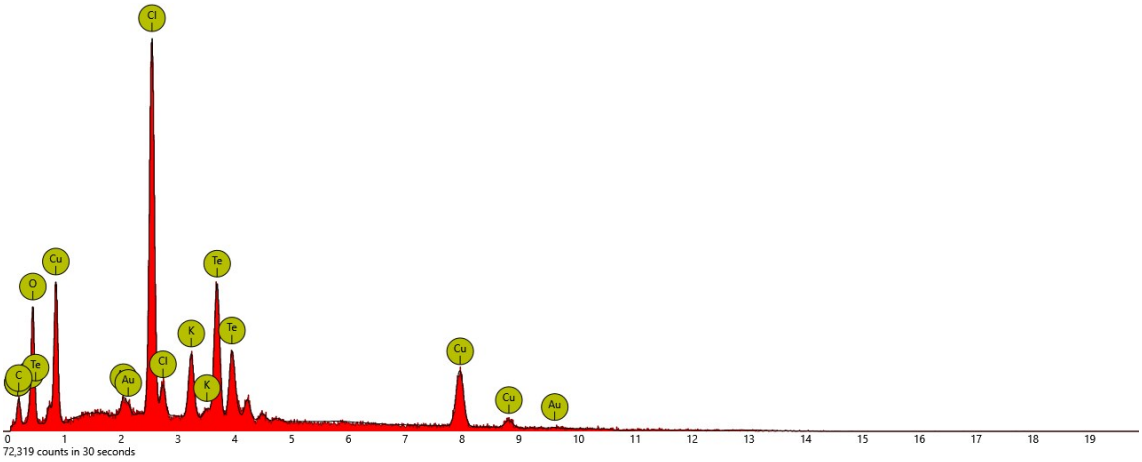
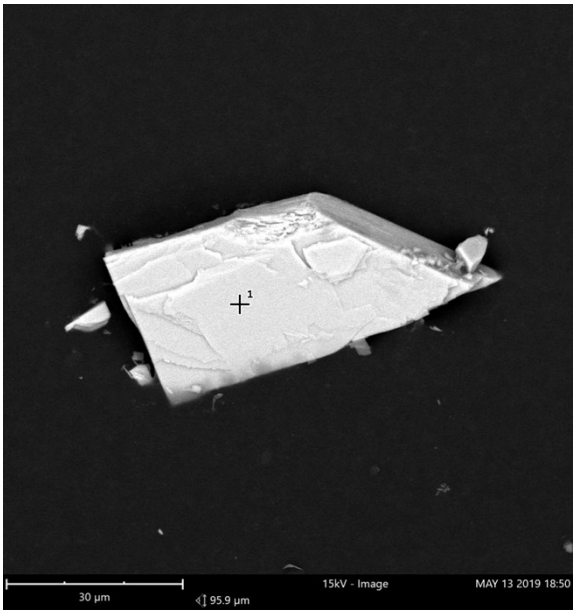


Figure S4.The corresponding EDX spectra for $K(NH_4)Cu_4Te_2Cl_6O_6$.



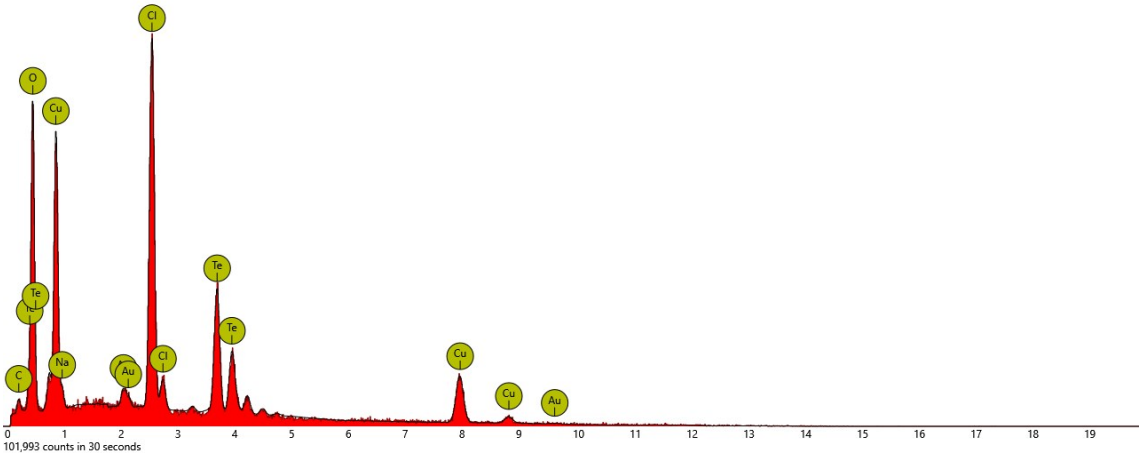


Figure S5.The corresponding EDX spectra for $NaCu_4Te_2Cl_5O_6$.

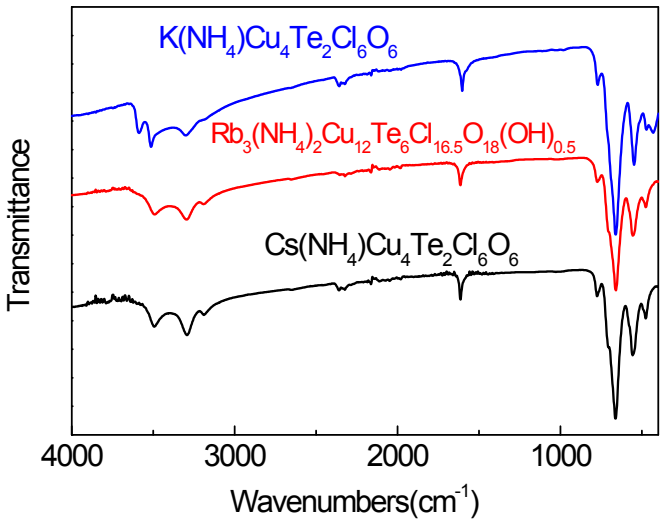


Figure S6. Infrared spectra of $Cs(NH_4)Cu_4Te_2Cl_6O_6$, $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$ and $K(NH_4)Cu_4Te_2Cl_6O_6$.

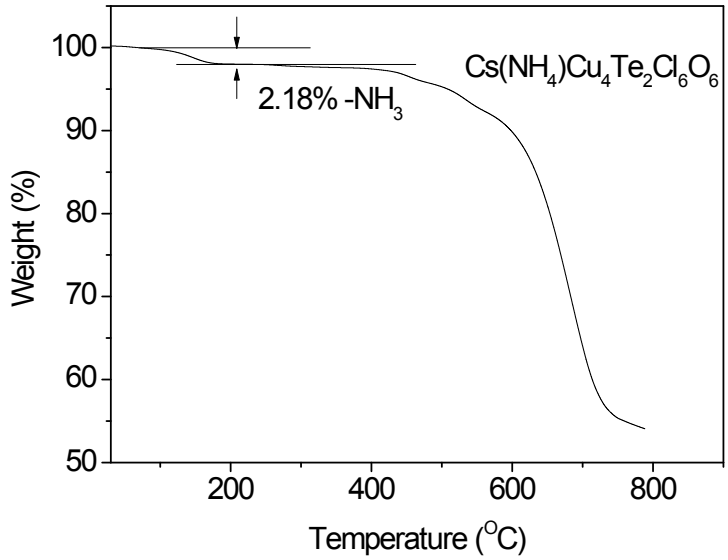


Figure S7. TGA diagram for $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

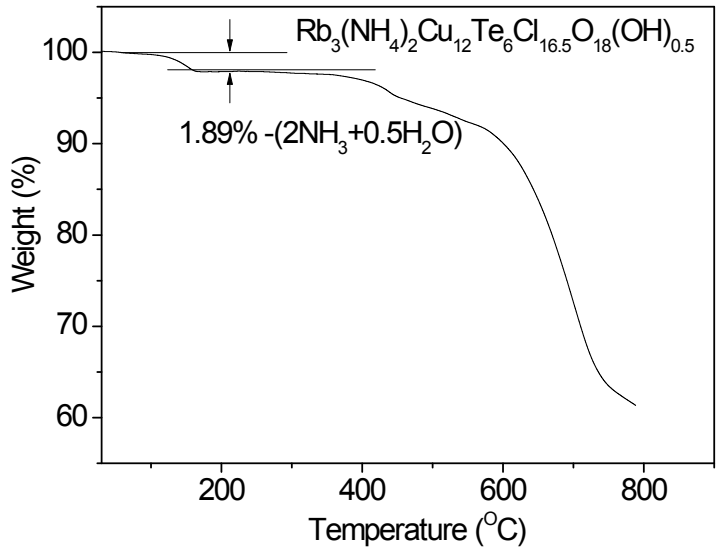


Figure S8. TGA diagram for $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

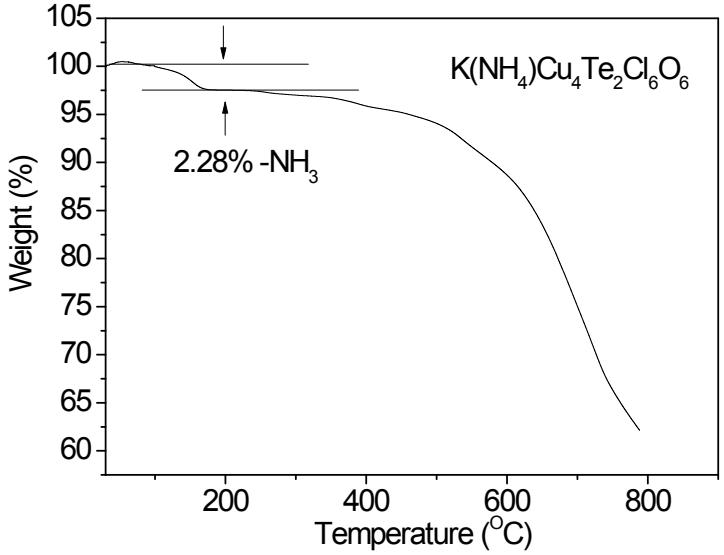


Figure S9. TGA diagram for $K(NH_4)Cu_4Te_2Cl_6O_6$.

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Cs(NH_4)Cu_4Te_2O_6Cl_6$.

Atom	Wyck.	*x*	*y*	*z*	Uiso*/Ueq	Occ.(<1)
Cs1	2e	0.75353(13)	0.75	0.02617(9)	0.0392(4)	1
Cu1	4f	0.03258(13)	0.57622(12)	0.37955(10)	0.0179(4)	1
Cu2	4f	0.46329(13)	0.57495(12)	0.61900(10)	0.0175(4)	1
Te1	2e	0.35206(10)	0.75	0.31460(7)	0.0142(3)	1
Te2	2e	-0.15340(10)	0.25	0.31454(7)	0.0136(3)	1
Cl1	4f	0.4725(3)	0.5188(3)	0.8264(2)	0.0312(9)	1
Cl2	2e	-0.2087(4)	0.75	0.3578(3)	0.0248(11)	1
Cl3	4f	0.0645(3)	0.4865(3)	0.1862(2)	0.0330(9)	1
Cl4	2e	0.6761(10)	0.75	0.6275(9)	0.143992	1
O1	2e	0.1497(10)	0.75	0.3612(8)	0.0199(19)	1
O2	4f	-0.0723(7)	0.4036(7)	0.4240(6)	0.0195(14)	1
O3	4f	0.4288(7)	0.5952(7)	0.4260(6)	0.0222(14)	1
O4	2e	0.3489(10)	0.75	0.6278(8)	0.0187(19)	1
N1	2e	0.7465	0.25	-0.0052	0.086179	1
H1	4f	0.7265	0.3236	0.0388	0.037995	1
H2	2e	0.8505	0.25	0.0081	0.037995	1
H3	2e	0.7122	0.25	-0.077	0.037995	1

Table S2. Harmonic displacement parameters obtained for the compound $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs1	0.0505(7)	0.0385(6)	0.0277(5)	0	0.0056(5)	0
Cu1	0.0228(7)	0.0122(6)	0.0191(6)	-0.0052(5)	0.0054(5)	-0.0017(4)
Cu2	0.0204(6)	0.0137(6)	0.0191(6)	0.0048(5)	0.0053(5)	0.0003(4)
Te1	0.0174(5)	0.0107(4)	0.0148(4)	0	0.0042(3)	0
Te2	0.0161(4)	0.0098(4)	0.0154(4)	0	0.0042(3)	0
Cl1	0.0480(17)	0.0261(14)	0.0212(12)	-0.0041(12)	0.0108(12)	0.0016(10)
Cl2	0.0204(18)	0.0259(19)	0.0280(17)	0	0.0047(14)	0
Cl3	0.0460(17)	0.0301(15)	0.0267(13)	-0.0024(13)	0.0162(12)	-0.0066(10)
Cl4	0.09087	0.185271	0.158729	0	0.031468	0

Table S3. Bond lengths **(**Å) and Band angles (degrees) of $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Atom1	Atom2	d	Band angles	degrees
Cs1	$Cl1^{i}$	3.574(3)	Cl2-Cu1-Cl3	112.33(10)
	$Cl1^{ii\wedge}$	3.666(3)	Cl2-Cu1-O1	84.4(2)
	$Cl1^{iii}$	3.666(3)	Cl2-Cu1-O2	97.26(19)
	$Cl1^{iv}$	3.574(3)	Cl2-Cu1-$O2^{xii}$	90.34(19)
	$Cl2^{v}$	3.447(3)	Cl3-Cu1-O1	93.1(3)

	$Cl3^{v}$	3.750(3)	Cl3-Cu1-O2	93.6(2)
	$Cl3^{vi}$	3.677(3)	Cl3-Cu1-$O2^{xii}$	157.09(19)
	$Cl3^{vii}$	3.677(3)	O1-Cu1-O2	171.8(3)
	$Cl3^{viii}$	3.750(3)	O1-Cu1-$O2^{xii}$	92.3(3)
	$Cl4^{i}$	4.124(10)	O2-Cu1-$O2^{xii}$	79.7(2)
Cu1	Cl2	2.587(3)	Cl1-Cu2-Cl4	103.6(2)
	Cl3	2.264(3)	Cl1-Cu2-O3	169.8(2)
	O1	1.916(5)	Cl1-Cu2-$O3^{iii}$	97.3(2)
	O2	1.925(6)	Cl1-Cu2-O4	93.9(3)
	$O2^{xii}$	2.040(6)	Cl4-Cu2-O3	86.4(3)
Cu2	Cl1	2.232(3)	Cl4-Cu2-$O3^{iii}$	98.8(3)
	Cl4	2.421(7)	Cl4-Cu2-O4	80.1(3)
	O3	2.006(6)	O3-Cu2-$O3^{iii}$	78.9(3)
	$O3^{iii}$	1.922(7)	O3-Cu2-O4	89.7(3)
	O4	1.895(5)	$O3^{iii}$-Cu2-O4	168.7(3)
Te1	O1	1.893(9)	O1-Te1-O3	93.7(3)
	O3	1.879(6)	O1-Te1-$O3^{ix}$	93.7(3)
	$O3^{ix}$	1.879(6)	O3-Te1-$O3^{ix}$	98.3(3)
Te2	O2	1.868(6)	O2-Te2-$O2^{x}$	98.0(2)
	$O2^{x}$	1.868(6)	O2-Te2-$O4^{xi}$	92.8(3)
	$O4^{xi}$	1.892(9)	$O2^{x}$-Te2-$O4^{xi}$	92.8(3)

Note: symmetry transformations used to generate equivalent atoms:
(i) x,y,z-1.(ii) -x+1,y+1/2,-z+1.(iii) -x+1,-y+1,-z+1.(iv) x,-y+3/2,z-1.(v) x+1,y,z.
(vi) -x+1,y+1/2,-z.(vii) -x+1,-y+1,-z.(viii) x+1,-y+3/2,z.(ix) x,-y+3/2,z.(x) x,-y+1/2,z (xi) -x,y-1/2,-z+1.(xii)-x,-y+1,-z+1.

Table 4. BVS of the atoms in $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

Atom	*BVS*
Cs1	0.959(3)
Cu1	2.003(13)
Cu2	2.228(14)
Te1	3.86(4)
Te2	3.94(4)
Cl1	0.748(4)
Cl2	0.579(3)
Cl3	0.656(4)
Cl4	0.669(8)
O1	2.23(3)
O2	2.16(2)
O3	2.16(2)
O4	2.29(3)
N1	3.01539(5)
H1	0.73758(2)

H2	0.72127(3)
H3	0.81896(3)

Table S5. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Atom	Wyck.	*x*	*y*	*z*	Uiso*/Ueq	Occ.(<1)
Rb1	2e	0.42794(7)	0.25	0.98399(19)	0.0414(6)	1
Rb2	2e	0.27861(8)	0.75	0.85184(19)	0.0430(7)	1
Rb3	2e	0.11843(10)	0.25	0.6873(2)	0.0605(9)	1
Cu1	4f	0.48845(5)	-0.42457(13)	0.37061(12)	0.0165(4)	1
Cu2	4f	0.16059(5)	0.57739(13)	0.07596(12)	0.0186(4)	1
Cu3	4f	0.16986(5)	0.42848(13)	0.33182(12)	0.0174(4)	1
Cu4	4f	0.00023(5)	0.57690(13)	0.12530(12)	0.0182(4)	1
Cu5	4f	0.32306(5)	0.07812(13)	0.24369(12)	0.0183(4)	1
Cu6	4f	0.34165(5)	-0.07199(13)	0.50202(12)	0.0179(4)	1
Te1	2e	0.09738(4)	0.75	0.31730(9)	0.0145(3)	1
Te2	2e	0.27164(4)	0.25	0.50233(9)	0.0143(3)	1
Te3	2e	0.06558(4)	0.75	-0.11387(9)	0.0143(3)	1
Te4	2e	0.45074(4)	-0.25	0.64509(9)	0.0141(3)	1
Te5	2e	0.21995(4)	0.25	0.07363(9)	0.0163(3)	1
Te6	2e	0.37884(4)	-0.25	0.22820(9)	0.0153(3)	1
Cl1	4f	0.49757(12)	-0.4808(3)	0.1685(3)	0.0294(9)	1
Cl2	4f	0.17600(12)	0.5202(3)	-0.1231(3)	0.0313(9)	1
Cl3	4f	0.33202(12)	0.0191(3)	0.0411(3)	0.0310(9)	1
Cl4	4f	-0.00895(16)	0.4994(4)	0.3214(3)	0.0500(13)	1
Cl5	2e	0.40966(15)	0.25	0.2974(4)	0.0255(12)	1
Cl6	4f	0.17144(13)	0.5183(3)	0.5273(3)	0.0344(10)	1
Cl7	2e	-0.08000(15)	0.75	0.0335(4)	0.0288(13)	1
Cl8	4f	0.34452(13)	0.0175(3)	0.6984(3)	0.0349(10)	1
Cl9	2e	0.24424(14)	0.75	0.1589(4)	0.0271(13)	1
Cl10	2e	0.0989(4)	0.25	0.2743(11)	0.057(4)	0.5
Cl11	2e	0.2687(4)	0.75	0.4564(9)	0.053(4)	0.5
Cl12	2e	0.4386(4)	0.25	0.5856(10)	0.052(4)	0.5
O1	2e	0.0378(3)	0.75	0.1895(9)	0.016(2)	1
O2	2e	0.3794(3)	-0.25	0.5551(9)	0.016(2)	1
O3	2e	0.2061(4)	0.25	0.3912(9)	0.021(2)	1
O4	2e	0.4484(3)	-0.25	0.3237(9)	0.015(2)	1
O5	4f	0.1325(3)	0.5957(7)	0.2480(6)	0.0185(15)	1
O6	2e	0.1225(4)	0.75	0.0217(9)	0.018(2)	1
O7	4f	-0.0302(3)	0.4053(8)	0.0440(7)	0.0219(16)	1
O8	4f	0.3036(3)	0.0951(7)	0.4229(6)	0.0205(16)	1
O9	4f	0.4740(3)	-0.4053(7)	0.5513(6)	0.0188(15)	1

O10	4f	0.1891(3)	0.4043(7)	0.1571(6)	0.0189(15)	1
O11	2e	0.2828(4)	0.25	0.1942(9)	0.022(2)	1
O12	4f	0.3547(3)	-0.0958(8)	0.3223(7)	0.0214(16)	1
O13	2e	0.0474(12)	0.25	0.478(3)	0.065(8)	0.5
H1o13	2e	0.0396	0.25	0.422	0.097995	0.5
N1	2e	0.5867(8)	0.25	0.0717(17)	0.074224	1
H1n1	2e	0.415	0.75	0.8522	0.097995	1
H2n1	4f	0.6043	0.3212	0.0439	0.097995	1
H3n1	2e	0.439	0.75	0.9819	0.097995	1
N2	2e	0.2463	0.25	0.7884	0.09494	1
H1n2	4f	0.2419	0.1425	0.7775	0.097995	1
H2n2	2e	0.28	0.25	0.8191	0.097995	1
H3n2	2e	0.2411	0.25	0.8704	0.097995	1

Table S6. Harmonic displacement parameters obtained for the compound $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb1	0.0471(10)	0.0314(10)	0.0503(12)	0	0.0247(9)	0
Rb2	0.0562(11)	0.0312(11)	0.0457(12)	0	0.0221(10)	0
Rb3	0.1045(18)	0.0348(12)	0.0509(14)	0	0.0439(13)	0
Cu1	0.0205(6)	0.0104(6)	0.0186(7)	0.0033(5)	0.0026(5)	0.0008(5)
Cu2	0.0233(6)	0.0123(7)	0.0197(7)	0.0049(5)	0.0011(5)	0.0033(5)
Cu3	0.0211(6)	0.0115(7)	0.0190(7)	0.0039(5)	0.0003(5)	0.0010(5)
Cu4	0.0235(6)	0.0120(7)	0.0187(7)	-0.0044(5)	0.0013(5)	-0.0012(5)
Cu5	0.0211(6)	0.0128(7)	0.0208(7)	0.0052(5)	0.0015(5)	0.0018(5)
Cu6	0.0211(6)	0.0119(7)	0.0205(7)	0.0050(5)	0.0022(5)	0.0014(5)
Te1	0.0163(4)	0.0117(5)	0.0150(5)	0	-0.0003(4)	0
Te2	0.0151(4)	0.0110(5)	0.0164(5)	0	0.0008(4)	0
Te3	0.0163(4)	0.0101(5)	0.0160(5)	0	0.0001(4)	0
Te4	0.0185(4)	0.0093(5)	0.0145(5)	0	0.0020(4)	0
Te5	0.0222(5)	0.0092(5)	0.0166(5)	0	-0.0008(4)	0
Te6	0.0215(5)	0.0086(5)	0.0149(5)	0	-0.0011(4)	0
Cl1	0.0448(16)	0.0227(15)	0.0209(15)	-0.0006(12)	0.0055(13)	-0.0010(12)
Cl2	0.0457(16)	0.0252(16)	0.0244(16)	-0.0053(13)	0.0098(13)	-0.0015(12)
Cl3	0.0472(17)	0.0247(16)	0.0217(15)	-0.0008(13)	0.0063(13)	0.0024(12)
Cl4	0.087(3)	0.043(2)	0.0207(17)	-0.0255(19)	0.0099(17)	0.0008(14)
Cl5	0.0266(18)	0.026(2)	0.023(2)	0	0.0017(16)	0
Cl6	0.0554(18)	0.0290(17)	0.0193(15)	0.0026(14)	0.0069(14)	-0.0037(12)
Cl7	0.0247(18)	0.030(2)	0.031(2)	0	0.0041(17)	0
Cl8	0.0548(18)	0.0290(17)	0.0207(15)	0.0099(14)	0.0045(14)	-0.0023(12)
Cl9	0.0198(17)	0.029(2)	0.032(2)	0	0.0009(16)	0
Cl10	0.058(6)	0.053(7)	0.060(7)	0	0.009(6)	0

Cl11	0.044(5)	0.076(8)	0.039(6)	0	0.003(5)	0

Table S7. Bond lengths (Å) and Band angles (degrees) of $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Atom1	Atom2	distances	Band angles	degrees
Rb1	$Cl1^{i}$	3.476(3)	Cl1-Cu1-$Cl12^{xii}$	100.1(3)
	$Cl1^{ii}$	3.355(3)	Cl1-Cu1-O4	93.2(3)
	$Cl1^{iii}$	3.355(3)	Cl1-Cu1-O9	170.7(2)
	$Cl1^{iv}$	3.476(3)	Cl1-Cu1-$O9^{xiii}$	96.9(2)
	$Cl3^{v}$	3.293(3)	$Cl12^{xii}$-Cu1-O4	80.7(3)
	$Cl3^{vi}$	3.293(3)	$Cl12^{xii}$-Cu1-O9	88.5(3)
	$Cl5^{v}$	3.412(4)	$Cl12^{xii}$-Cu1-$O9^{xiii}$	98.7(2)
Rb2	$Cl2^{v}$	3.334(3)	O4-Cu1-O9	91.5(3)
	$Cl2^{vii}$	3.334(3)	O4-Cu1-$O9^{xiii}$	169.8(4)
	$Cl3^{i}$	3.353(3)	O9-Cu1-$O9^{xiii}$	78.3(3)
	$Cl3^{vi}$	3.353(3)	Cl2-Cu2-Cl9	103.54(12)
	$Cl8^{viii}$	3.468(3)	Cl2-Cu2-O5	166.9(2)
	$Cl8^{ix}$	3.468(3)	Cl2-Cu2-O6	92.7(3)
	$Cl9^{v}$	3.468(5)	Cl2-Cu2-O10	97.6(2)
Rb3	$Cl2^{v}$	3.397(3)	Cl9-Cu2-O5	89.5(2)
	$Cl2^{vi}$	3.397(3)	Cl9-Cu2-O6	86.1(2)
	$Cl4^{x}$	3.543(4)	Cl9-Cu2-O10	97.2(2)
	$Cl4^{xi}$	3.543(4)	O5-Cu2-O6	89.5(4)
	Cl6	3.355(3)	O5-Cu2-O10	79.2(3)
	$Cl6^{ix}$	3.355(3)	O6-Cu2-O10	168.2(4)
	$Cl7^{x}$	3.222(5)	Cl6-Cu3-Cl10	114.4(3)
	O13	2.65(3)	Cl6-Cu3-O3	93.4(3)
Cu1	Cl1	2.245(3)	Cl6-Cu3-O5	94.8(2)
	$Cl12^{xii}$	2.413(7)	Cl6-Cu3-O10	159.0(2)
	O4	1.920(5)	Cl10-Cu3-O3	78.1(3)
	O9	2.002(7)	Cl10-Cu3-O5	97.9(3)
	$O9^{xiii}$	1.951(7)	Cl10-Cu3-O10	86.5(3)
Cu2	Cl2	2.255(3)	O3-Cu3-O5	171.8(3)
	Cl9	2.664(3)	O3-Cu3-O10	93.1(4)
	O5	2.039(7)	O5-Cu3-O10	79.5(3)
	O6	1.898(5)	Cl4-Cu4-Cl7	112.24(14)
	O10	1.904(7)	Cl4-Cu4-O1	92.0(3)
Cu3	Cl6	2.229(3)	Cl4-Cu4-O7	94.4(2)
	Cl10	2.422(8)	Cl4-Cu4-$O7^{xiv}$	159.7(2)
	O3	1.938(5)	Cl7-Cu4-O1	86.2(2)
	O5	1.951(7)	Cl7-Cu4-O7	95.8(2)
	O10	1.983(7)	Cl7-Cu4-$O7^{xiv}$	87.9(2)
Cu4	Cl4	2.238(4)	O1-Cu4-O7	172.0(4)
	Cl7	2.630(3)	O1-Cu4-$O7^{xiv}$	92.0(3)
	O1	1.925(5)	O7-Cu4-$O7^{xiv}$	80.4(3)

	O7	1.909(7)	Cl3-Cu5-Cl5	100.11(12)
	O7^{xiv}	2.033(7)	Cl3-Cu5-O8	167.7(2)
Cu5	Cl3	2.255(3)	Cl3-Cu5-O11	92.7(3)
	Cl5	2.661(3)	Cl3-Cu5-O12	97.4(2)
	O8	2.025(7)	Cl5-Cu5-O8	91.8(2)
	O11	1.907(5)	Cl5-Cu5-O11	86.5(2)
	O12	1.925(7)	Cl5-Cu5-O12	97.6(2)
Cu6	Cl8	2.234(3)	O8-Cu5-O11	91.0(4)
	Cl11^{xv}	2.437(7)	O8-Cu5-O12	77.8(3)
	O2	1.934(5)	O11-Cu5-O12	168.1(4)
	O8	1.938(7)	Cl8-Cu6-Cl11^{xv}	111.7(3)
	O12	1.985(7)	Cl8-Cu6-O2	94.8(3)
Te1	O1	1.869(8)	Cl8-Cu6-O8	93.9(2)
	O5	1.863(7)	Cl8-Cu6-O12	161.2(2)
	O5^{xvi}	1.863(7)	Cl11 ^{xv}-Cu6-O2	78.7(3)
Te2	O3	1.875(9)	Cl11^{xv}-Cu6-O8	98.3(2)
	O8	1.880(7)	Cl11^{xv}-Cu6-O12	86.5(3)
	O8^{ix}	1.880(7)	O2-Cu6-O8	171.3(3)
Te3	O6	1.879(9)	O2-Cu6-O12	93.2(3)
	O7^{xvii}	1.876(7)	O8-Cu6-O12	78.4(3)
	O7^{xiv}	1.876(7)	O1-Te1-O5	94.3(3)
Te4	O2	1.891(8)	O1-Te1-O5^{xvi}	94.3(3)
	O9	1.873(7)	O5-Te1-O5^{xvi}	99.5(3)
	O9^{xviii}	1.873(7)	O3-Te2-O8	95.4(3)
Te5	O10	1.885(7)	O3-Te2-O8^{ix}	95.4(3)
	O10^{ix}	1.885(7)	O8-Te2-O8^{ix}	98.8(3)
	O11	1.881(9)	O6-Te3-O7^{xvii}	92.1(3)
Te6	O4	1.877(8)	O6-Te3-O7^{xiv}	92.1(3)
	O12	1.876(7)	O7^{xvii}-Te3-O7^{xiv}	99.4(3)
	O12^{xviii}	1.876(7)	O2-Te4-O9	93.4(3)
			O2-Te4-O9^{xviii}	93.4(3)
			O9-Te4-O9^{xviii}	99.6(3)
			O10-Te5-O10^{ix}	97.9(3)
			O10-Te5-O11	91.5(3)
			O10^{ix}-Te5-O11	91.5(3)
			O4-Te6-O12	92.4(3)
			O4-Te6-O12^{xviii}	92.4(3)
			O12-Te6-O12^{xviii}	98.4(3)

Note: symmetry transformations used to generate equivalent atoms:

(i) x,y+1,z+1
(ii) -x+1,y+1/2,-z+1
(iii) -x+1,-y,-z+1
(iv) x,-y-1/2,z+1
(v) x,y,z+1

(vi) x,-y+1/2,z+1
(vii) -x+1,y-1/2,-z+2
(viii) x,-y+3/2,z+1
(ix) x,y+1,z
(x) x,-y+1/2,z
(xi) -x+1,-y+1,-z+1
(xii) -x,y-1/2,-z+1
(xiii) -x,-y+1,-z+1
(xiv) -x+1,y-1/2,-z+1
(xv) -x+1,-y-1,-z+1
(xvi) -x,-y+1,-z
(xvii) x,y-1,z
(xviii)x,-y+3/2,z

Table S8. BVS of the atoms in $Rb_3(NH_4)_2Cu_{12}Te_6Cl_{16.5}O_{18}(OH)_{0.5}$.

Atom	*BVS**
Rb1	0.997(4)
Rb2	0.948(3)
Rb3	1.138(14)
Cu1	1.987(13)
Cu2	2.029(14)
Cu3	2.003(14)
Cu4	2.032(14)
Cu5	2.004(14)
Cu6	2.008(14)
Te1	4.06(5)
Te2	3.91(5)
Te3	3.93(5)
Te4	3.91(4)
Te5	3.86(5)
Te6	3.94(5)
Cl1	0.773(5)
Cl2	0.794(5)
Cl3	0.829(5)
Cl4	0.615(5)
Cl5	0.463(3)
Cl6	0.688(5)
Cl7	0.579(4)
Cl8	0.641(5)
Cl9	0.443(2)
Cl10	0.639(9)
Cl11	0.614(8)
Cl12	0.655(9)
O1	2.29(3)
O2	2.19(3)
O3	2.23(3)

O4	2.27(3)
O5	2.15(3)
O6	2.32(3)
O7	2.16(3)
O8	2.12(3)
O9	2.15(3)
O10	2.19(3)
O11	2.29(3)
O12	2.19(3)
O13	0.84(3)

Table S9. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $K(NH_4)Cu_4Te_2Cl_6O_6$.

Atom	Wyck.	*x*	*y*	*z*	Uiso*/Ueq	Occ.(<1)
K1	4i	0.367(4)	0	0.058(4)	0.041(5)	0.1
N1	4i	0.367(4)	0	0.058(4)	0.041(5)	0.5
H1	8j	0.3711	0.0848	0.0398	0.04169	0.5
H2	4i	0.3065	0	0.1337	0.037995	0.5
H3	4i	0.7449	0	0.9837	0.037995	0.5
K1'	4i	0.431(2)	0	0.067(2)	0.041(5)	0.4
Cu1	8j	1.1838(3)	0.1750(3)	0.3779(3)	0.0200(8)	1
Te1	4i	0.8564(2)	0	0.30938(18)	0.0145(5)	1
Cl1	8j	1.1251(10)	0.2442(9)	0.1691(7)	0.073(3)	1
Cl2	4i	0.4196(16)	0	0.3683(13)	0.079(5)	1
O1	4i	1.0618(19)	0	0.3632(16)	0.012(4)	1
O2	8j	0.8049(15)	0.1533(14)	0.4240(13)	0.021(3)	1

Table S10. Harmonic displacement parameters obtained for the compound $K(NH_4)Cu_4Te_2Cl_6O_6$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	0.0185(14)	0.0123(13)	0.0291(15)	-0.0059(10)	-0.0018(11)	0.0022(11)
Te1	0.0137(9)	0.0086(9)	0.0212(10)	0	0.0008(7)	0
Cl1	0.099(6)	0.065(5)	0.055(4)	-0.050(5)	-0.043(4)	0.029(4)
Cl2	0.104(10)	0.051(7)	0.083(9)	0	0.027(8)	0

Table S11. Bond lengths **(**Å) and Band angles (degrees) of $K(NH_4)Cu_4Te_2Cl_6O_6$.

Atom1	Atom2	distances	Band angles	degrees
K1	$Cl1^{i}$	3.28(3)	$Cl1\text{-}Cu1\text{-}Cl2^{viii}$	108.1(4)

	$Cl1^{ii}$	3.42(3)	Cl1-Cu1-O1	92.4(5)
	$Cl1^{iii}$	3.26(3)	Cl1-Cu1-$O2^{ix}$	164.8(4)
	$Cl1^{iv}$	3.26(3)	Cl1-Cu1-$O2^{x}$	96.5(4)
	$Cl1^{v}$	3.28(3)	$Cl2^{viii}$-Cu1-O1	85.8(5)
	$Cl1^{vi}$	3.42(3)	$Cl2^{viii}$-Cu1-$O2^{ix}$	86.9(5)
	Cl2	3.13(4)	$Cl2^{viii}$-Cu1-$O2^{x}$	94.2(4)
K1'	$Cl1^{i}$	3.635(18)	O1-Cu1-$O2^{ix}$	90.8(6)
	$Cl1^{ii}$	3.058(16)	O1-Cu1-$O2^{x}$	170.6(6)
	$Cl1^{iii}$	3.360(18)	$O2^{ix}$-Cu1-$O2^{x}$	79.8(5)
	$Cl1^{iv}$	3.360(18)	O1-Te1-O2	93.5(5)
	$Cl1^{v}$	3.635(18)	O1-Te1-$O2^{vii}$	93.5(5)
	$Cl1^{vi}$	3.058(16)	O2-Te1-$O2^{vii}$	97.1(6)
	Cl2	3.02(3)		
Cu1	Cl1	2.239(8)		
	$Cl2^{viii}$	2.612(11)		
	O1	1.926(10)		
	$O2^{ix}$	1.996(13)		
	$Cl2^{viii}$	2.612(11)		
Te1	O1	1.870(17)		
	O2	1.869(13)		
	$O2^{vii}$	1.869(13)		

Note: symmetry transformations used to generate equivalent atoms:
(i)x-1,y,z
(ii) x-1/2,y-1/2,z
(iii) -x+3/2,y-1/2,-z
(iv) -x+3/2,-y+1/2,-z
(v) x-1,-y,z
(vi) x-1/2,-y+1/2,z
(vii)x,-y,z
(viii) x+1,y,z
(ix) -x+2,y,-z+1
(x) x+1/2,-y+1/2,z

Table S12. BVS of the atoms in $K(NH_4)Cu_4Te_2Cl_6O_6$.

Atom	*BVS**
K1	0.89(3)
K1'	1.03(2)
Cu1	2.03(3)
Te1	4.01(9)
Cl1	0.712(12)
Cl2	0.505(11)
O1	2.28(6)
O2	2.18(5)

Table S13. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of $NaCu_4Te_2Cl_5O_6$.

Atom	Wyck.	*x*	*y*	*z*	Uiso*/Ueq	Occ.(<1)
Na1	2c	0	0	0.5	0.045(5)	1
Cu1	8j	-0.14895(18)	0.17339(15)	0.12025(14)	0.0196(5)	1
Te1	4i	0.20837(14)	0	0.18445(11)	0.0160(4)	1
Cl1	8j	-0.0088(9)	0.2485(8)	0.3201(7)	0.0058(10)	0.375
Cl1'	8j	-0.0494(9)	0.2350(8)	0.3290(8)	0.0058(10)	0.375
Cl2	4i	0.6160(10)	0	0.1327(8)	0.018(3)	0.5
Cl3	4i	0.7225(18)	0	0.4803(16)	0.076(7)	0.5
O1	4i	-0.0181(14)	0	0.1380(11)	0.022(3)	1
O2	8j	0.2189(10)	0.1560(8)	0.0738(8)	0.0207(19)	1

Table S14. Harmonic displacement parameters obtained for the compound $NaCu_4Te_2Cl_5O_6$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.055(8)	0.034(7)	0.047(8)	0	0.016(7)	0
Cu1	0.0247(9)	0.0140(8)	0.0191(9)	0.0055(6)	0.0044(7)	-0.0003(6)
Te1	0.0185(6)	0.0120(6)	0.0158(6)	0	0.0015(5)	0
Cl2	0.028(5)	0.016(4)	0.015(4)	0	0.012(4)	0
Cl3	0.075(11)	0.059(9)	0.087(12)	0	0.011(9)	0

Table S15. Bond lengths **(**Å) and Band angles (degrees) of $NaCu_4Te_2Cl_5O_6$.

Atom1	Atom2	distances	Band angles	degrees
Na1	Cl1	2.985(8)	Cl1-Cu1-Cl1'	10.3(3)
	$Cl1^{i}$	2.985(8)	Cl1-Cu1-$Cl2^{iv}$	111.1(3)
	$Cl1^{ii}$	2.985(8)	Cl1-Cu1-O1	91.1(4)
	$Cl1^{iii}$	2.985(8)	Cl1-Cu1-$O2^{vi}$	159.6(3)
	Cl1'	2.798(8)	Cl1-Cu1-$O2^{vii}$	96.6(3)
	$Cl1'^{i}$	2.798(8)	Cl1'-Cu1-$Cl2^{iv}$	101.3(3)
	$Cl1'^{ii}$	2.798(8)	Cl1'-Cu1-O1	93.5(4)
	$Cl1'^{iii}$	2.798(8)	Cl1'-Cu1-$O2^{vi}$	168.5(3)
	$Cl3^{iv}$	2.319(16)	Cl1'-Cu1-$O2^{vii}$	94.9(3)
	$Cl3^{v}$	2.319(16)	$Cl2^{iv}$-Cu1-O1	85.2(3)
Cu1	Cl1	2.256(7)	$Cl2^{iv}$-Cu1-$O2^{vi}$	89.2(3)
	Cl1'	2.235(8)	$Cl2^{iv}$-Cu1-$O2^{vii}$	96.5(3)
	$Cl2^{iv}$	2.599(7)	O1-Cu1-$O2^{vi}$	92.2(4)
	O1	1.934(7)	O1-Cu1-$O2^{vii}$	170.9(5)
	$O2^{vii}$	2.003(8)	$O2^{vi}$-Cu1-$O2^{vii}$	79.0(3)

	$O2^{viii}$	1.925(8)	O1-Te1-O2	93.1(3)
Te1	O1	1.860(12)	$O1-Te1-O2^{iii}$	93.1(3)
	O2	1.883(8)	$O2-Te1-O2^{iii}$	100.1(4)
	$O2^{iii}$	1.883(8)		

Note: symmetry transformations used to generate equivalent atoms:

(i) -x,y,-z+1
(ii) -x,-y,-z+1
(iii) x,-y,z
(iv) x-1,y,z
(v) -x+1,y,-z+1
(vi) -x,y,-z
(vii) x-1/2,-y+1/2,z

Table S16. BVS of the atoms in $NaCu_4Te_2Cl_5O_6$.

Atom	*BVS*
Na1	1.050(19)
Cu1	1.806(16)
Te1	3.95(6)
Cl1	0.605(10)
Cl1'	0.704(12)
Cl2	0.395(6)
Cl3	0.63(3)
O1	2.30(4)
O2	2.15(3)

* (R, b) parameters being forCs^{+}-Cl (2.791, 0.37), Rb^{+}-Cl (2.652, 0.37), K^{+}-Cl (2.519, 0.37), Na^{+}-Cl (2.15, 0.37), Cu^{2+}-Cl (2.0, 0.37),Cu^{2+}-O (1.649, 0.37), Te^{4+}-O (1.977, 0.37), N^{3+}-H (0.569, 0.94),

Table S17. Geometrical Parameters Associated with the M- O•••O -M Super-Supperexchange Paths of $Cs(NH_4)Cu_4Te_2Cl_6O_6$.

	Cu1-Cu2	Cu1-Cu2	Cu1-Cu2	Cu1-Cu2	Average
<M–O2•••O4	143.9(3)	143.9(3)	102.5(2)	102.5(2)	123.2(3)
<O2•••O4-M	89.4(1)	150.3(1)	89.4(1)	150.3(1)	119.9(1)
M•••M	4.476(1)	6.269(2)	4.047(1)	5.162(2)	4.989(2)
O2•••O4	2.722(9)	2.722(9)	2.722(9)	2.722(9)	2.722(9)

	Cu1-Cu2	Cu1-Cu2	Cu1-Cu2	Cu1-Cu2	Average
<M–O1•••O3	89.6(1)	89.6(1)	148.5(1)	148.5(1)	119.1(1)
<O1•••O3-M	142.7(3)	104.4(2)	142.7(3)	104.4(2)	123.6(2)
M•••M	4.538(2)	4.047(1)	6.297(2)	5.162(2)	5.011(2)

O1•••O3	2.753(9)	2.753(9)	2.753(9)	2.753(9)	2.753(9)

Table S18. Geometrical Parameters Associated with the M- O•••O - M Super-Supperexchange Paths of $K(NH_4)Cu_4Te_2Cl_6O_6$.

	Cu1-Cu1	Cu1-Cu1	Cu1-Cu1	Cu1-Cu1	Average
<M–O1•••O2	90.8(3)	90.8(3)	150.2(2)	150.2(2)	120.5(3)
<O1•••O2-M	144.1(6)	104.0(5)	144.1(6)	104.0(5)	124.1(6)
M•••M	4.583(4)	4.062(5)	5.169(1)	6.324(4)	5.035(5)
O1•••O2	2.722(2)	2.722(2)	2.722(2)	2.722(2)	2.722(2)