Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Pressure-induced Jahn-Teller Switch in the Homoleptic Hybrid Perovskite $[(CH_3)_2NH_2]Cu(HCOO)_3$: Orbital Reodering by Unconventional Degrees of Freedom

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## Supplementary Information

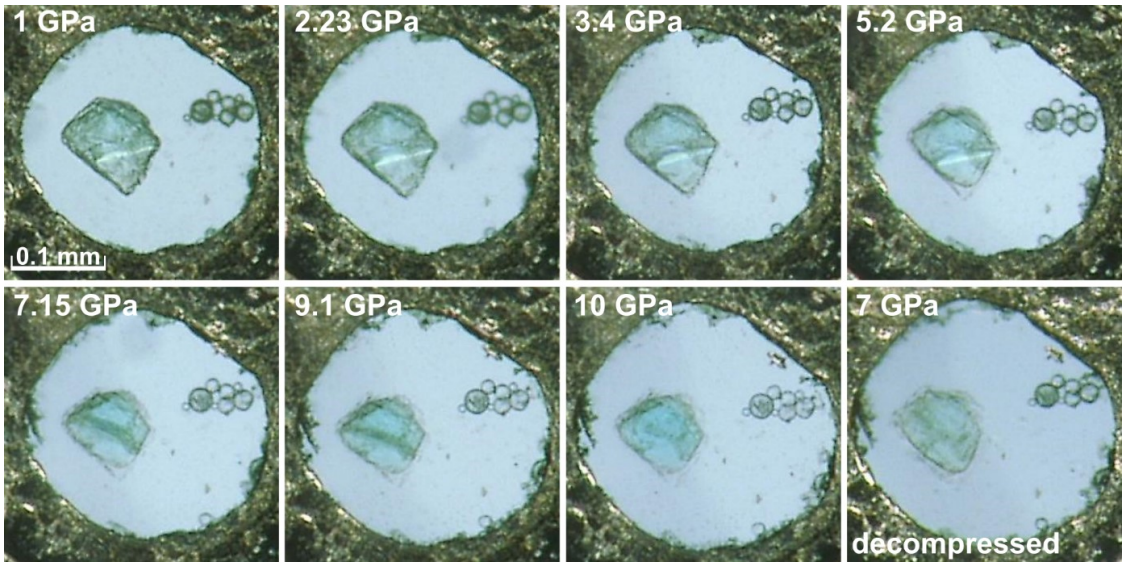



***Figure S1.*** Single crystal of [Cu(HCOO)3]H2N(CH3)2 in DAC. Ruby spheres are the spheres located by the edge.

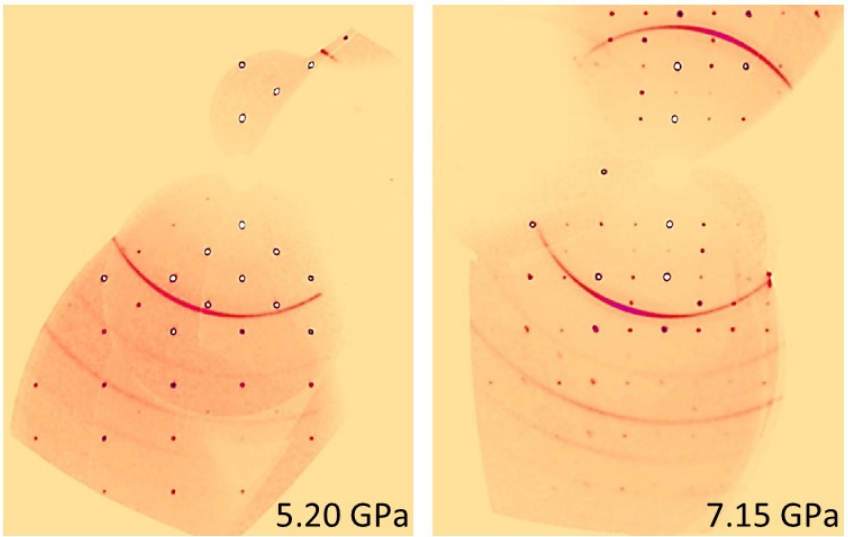



***Figure S2.*** (0kl) diffraction plane for a single crystal of $[(CH_3)_2NH_2]Cu(HCOO)_3$ at 5.20 and 7.15 GPa.

***Table S1.*** Selected single crystal diffraction data and refinements details for $[(CH_3)_2NH_2]Cu(HCOO)_3$ at 295 K.

| Pressure (GPa) | 0.00001 GPa | 1.0 | 2.23 | 3.40 | 3.8 |
|---|---|---|---|---|---|
| Loading | - | A | A | A | B |
| Crystal size | 0.6x0.3x0.3 | 0.1x0.08x0.05 | 0.1x0.08x0.05 | 0.1x0.08x0.05 | 0.11x0.0.072x0.0 0.056 |
| phase | α | α | α | α | α |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | *I*2/*a* | *I*2/*a* | *I*2/*a* | *I*2/*a* | *I*2/*a* |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.49647 |
| a (Å) | 8.8330(4) | 8.6895(13) | 8.5019(14) | 8.323(3) | 8.2878(9) |
| b (Å) | 8.7093(4) | 8.5925(10) | 8.5043(10) | 8.4733(14) | 8.4645(6) |
| c (Å) | 11.4145(5) | 11.3323(4) | 11.2256(4) | 11.1183(7) | 11.0942(3) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| β (°) | 96.224(4) | 95.623(7) | 95.055(7) | 94.553(12) | 94.521(4) |
| γ (°) | 90 | 90 | 90 | 90 | 90 |
| Volume (Å$^3$) | 872.93(7) | 842.05(16) | 808.48(17) | 781.7(3) | 775.86(10) |
| Z / Z' | 4/1 | 4/1 | 4/1 | 4/1 | 4/1 |
| Min/max hkl | -11/12, -11/12, -15/15 | -6/5, -8/5, -14/8 | -5/5, -8/5, -8/13 | -4/5, -8/6, -8/13 | -7/9, -9/10, -17/17 |
| 2θ ranges (°) | 7.182 – 59.158 | 6.684 – 52.856 | 6.79 – 51.294 | 6.052 – 51.864 | 5.152 – 52.944 |
| Collected/unique | 8550 / 1133 | 838 / 254 | 771 / 237 | 710 / 229 | 1139 / 688 |
| $r_{int}$ / % | 4.32 | 3.21 | 2.87 | 4.05 | 1.57 |
| Completeness (%) | 99.6 | 29.26 | 30.50 | 29.78 | 29.28 |
| GOF *w* | 1.140 | 1.115 | 1.103 | 1.108 | 1.091 |
| $R_1$(F) % [I ≥2σ] | 2.36 | 3.39 | 3.35 | 4.38 | 3.59 |
| $R_1$(F) % [all] | 2.89 | 4.29 | 4.36 | 5.24 | 4.15 |
| $w_1/w_2$ | 0.03 / 0.40 | 0.06 / 1.40 | 0.033 / 5.91 | 0.06 / 1.54 | 0.082 / 0 |
| peak/hole (eÅ$^{-3}$) | 0.32 / -0.58 | 0.25 / -0.28 | 0.23 / -0.26 | 0.34 / -0.33 | 0.39 / -0.41 |

***Table S2.*** Selected single crystal diffraction data and refinements details for $[(CH_3)_2NH_2]Cu(HCOO)_3$ at 295 K.

| Pressure (GPa) | 5.20 | 7.15 | 8.30 | 9.10 |
|---|---|---|---|---|
| Loading | A | A | B | A |
| Crystal size | 0.1x0.08x0.05 | 0.1x0.08x0.05 | 0.11x0.072x0.056 | 0.1x0.08x0.05 |
| phase | α | γ | γ | γ |
| Crystal system | monoclinic | triclinic | triclinic | triclinic |
| Space group | *I*2/*a* | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| λ (Å) | 0.71073 | 0.71073 | 0.49647 | 0.71073 |
| a (Å) | 8.086(4) | 7.2638(16) | 7.2432(13) | 7.2332(8) |
| b (Å) | 8.466(2) | 8.5726(15) | 8.5444(11) | 8.5452(10) |
| c (Å) | 10.9541(9) | 11.2929(17) | 11.2169(19) | 11.085(4) |
| α (°) | 90 | 92.384(13) | 92.441(13) | 92.908(17) |
| β (°) | 94.215(17) | 101.797(16) | 102.055(15) | 102.278(18) |
| γ (°) | 90 | 91.352(16) | 91.298(13) | 91.268(10) |
| Volume (Å$^3$) | 747.8(4) | 687.4(2) | 677.92(19) | 668.2(3) |
| Z / Z' | 4/1 | 4/2 | 4/2 | 4/2 |
| Min/max hkl | -4/4, -7/5, -13/7 | -6/6, -10/7, -15/15 | -12/12, -14/15, -12/9 | -8/4, -7/6, -4/7 |
| 2θ ranges (°) | 6.088 – 50.962 | 3.688 – 56.738 | 3.334 – 55.312 | 4.776 – 51.684 |
| Collected/unique | 350 / 120 | 3829 / 737 | 3954 / 2430 | 1301 / 432 |
| $r_{int}$ / % | 2.45 | 5.96 | 6.41 | 4.38 |
| Completeness (%) | 17.19 | 21.38 | 47.1 | 17.69 |
| GOF *w* | 1.115 | 1.063 | 1.078 | 1.118 |
| $R_1$ (F) % [I ≥2σ] | 3.36 | 7.67 | 5.08 | 5.47 |
| $R_1$ (F) % [all] | 3.95 | 13.06 | 10.64 | 8.66 |
| $w_1/w_2$ | 0.061 / 10.3 | 0.142 / 10.3 | 0.055 / 0 | 0.095 / 1.32 |
| peak/hole (eÅ$^{-3}$) | 0.19 / -0.22 | 0.67 / -0.66 | 0.7 / -0.5 | 0.34 / -0.31 |

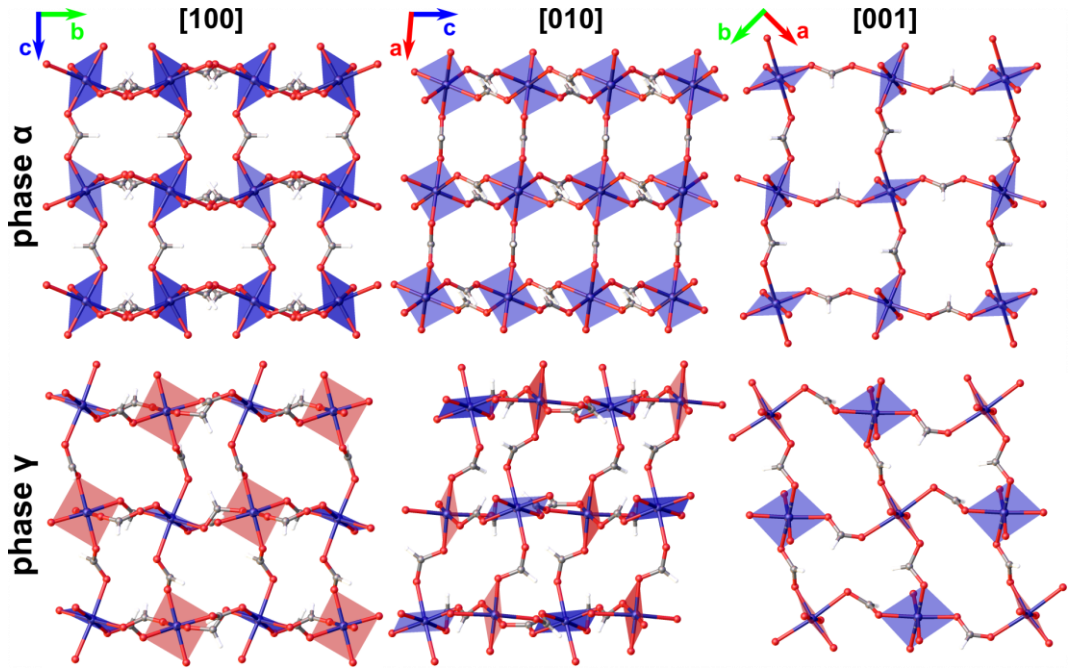



***Figure S3.*** Fragments of $[(CH_3)_2NH_2]Cu(HCOO)_3$ structure in the α and γ phase viewed along the main crystallographic directions. Equatorial planes perpendicular to JT axes are highlighted by the blue and red square planes.

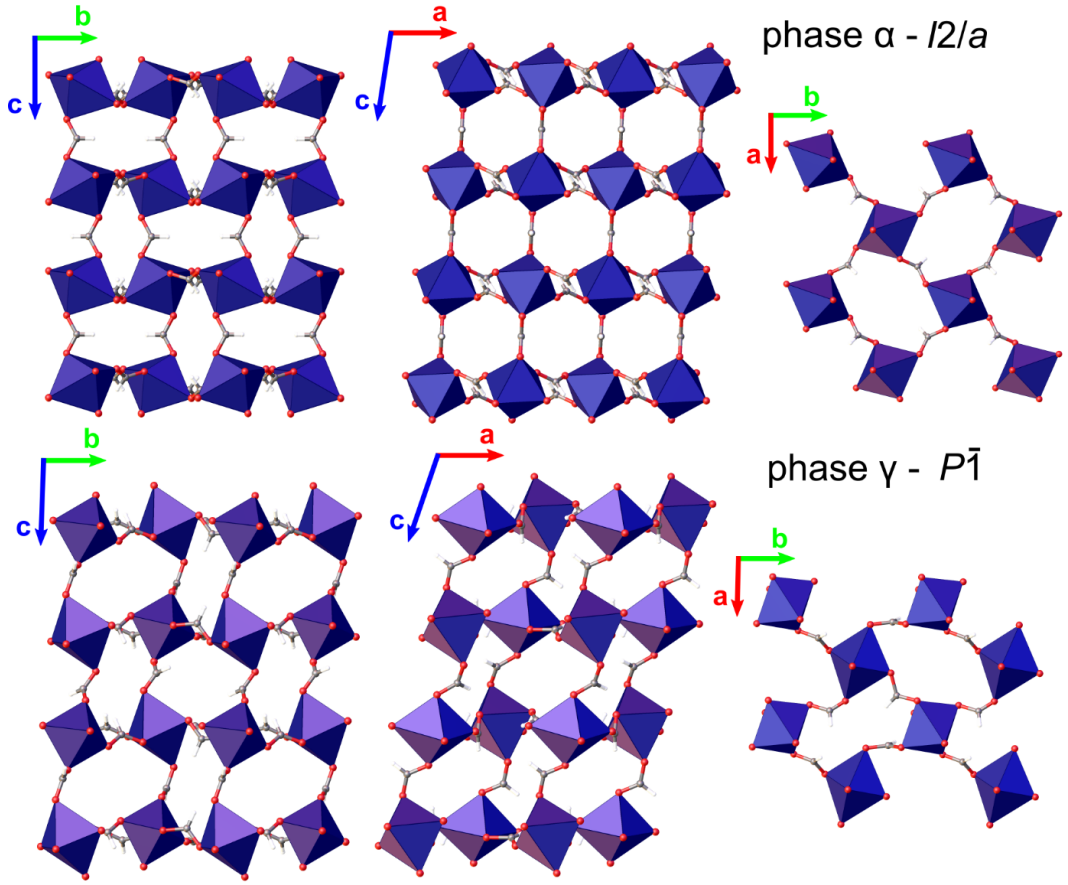



***Figure S4.*** View along the *a*, *b*, and *c* crystallographic axis of the $CuO_6$ octahedra bridged by formate $[HCOO^-]$ ligands in the α and γ phases. The dimethylammonium $[H_2N(CH_3)_2]^+$ A site cations were omitted for sake of clarity.

***Table S3.*** Structure of the *P*4/mmm parent cell.

| Atom | x | y | z | g |
|---|---|---|---|---|
| Cu1 | 0.000000 | 0.000000 | 0.000000 | 0.0625 |
| O1 | 0.000000 | 0.000000 | 0.305817 | 0.1250 |
| O2 | 0.321708 | 0.000000 | 0.000000 | 0.2500 |
| C1 | 0.500000 | 0.000000 | 0.000000 | 0.1250 |
| C2 | 0.000000 | 0.000000 | 0.500000 | 0.0625 |
| C3 | 0.500000 | 0.500000 | 0.597350 | 0.1250 |
| N1 | 0.500000 | 0.500000 | 0.500000 | 0.0625 |

***Table S4.*** Mode amplitudes refined as function of pressure for the monoclinic *I*2/a α-phase from single crystal x-ray data.

| Mode | Normalization factor/direction | 0.0004 GPa | 1.0 GPa | 2.23 GPa | 3.40 GPa | 4.75 GPa | 5.20 GPa |
|---|---|---|---|---|---|---|---|
| Γ1+ Oc | 0.0435/(0,0,1) | -0.0046(58) | 0.002(21) | -0.038(16) | -0.032(19) | -0.053(77) | -0.0578(26) |
| Γ1+ $O_{ab}$ | 0.0283/(1,1,0) | -0.0324(62) | -0.032(32) | -0.040(24) | -0.022(34) | -0.119(26) | -0.044(44) |
| Γ1+ $C_{DMA}$ | 0.0435/(0,0,1) | 0.207(11) | 0.197(33) | 0.305(24) | 0.350(32) | 0.324(16) | 0.495(38) |
| Γ4+ $O_{ab}$ | 0.0283/(1,-1,0) | -0.0146(66) | -0.006(35) | -0.105(25) | -0.190(36) | -0.123(13) | -0.159(58) |
| Γ5+ Oc | 0.0566/(1,0,0) | -0.1320(61) | -0.134(36) | -0.116(25) | -0.148(37) | -0.164(12) | -0.080(52) |
| Γ5+ $O_{ab}$ | 0.0308/(0,0,1) | -0.2026(64) | -0.267(25) | -0.249(17) | -0.303(21) | -0.2486(86) | -0.338(30) |
| Γ5+ $C_{DMA}$ | 0.0566/(1,0,0) | -1.9553(99) | -2.171(55) | -1.946(43) | -2.034(67) | -1.988(22) | -1.888(75) |
| A2+ $O_{ab}$ | 0.0283/(1,1,0) | -0.5967(62) | -0.477(36) | -0.471(27) | -0.356(33) | -0.302(11) | -0.265(50) |
| A2+ $C_{ab}$ | 0.0400/(1,1,0) | 0.4230(95) | 0.356(59) | 0.331(42) | 0.199(56) | 0.258(16) | 0.125(90) |
| A3+ $O_{ab}$ | 0.0283/(1,-1,0) | -1.9606(65) | -1.982(32) | -1.993(24) | -2.045(34) | -2.050(12) | -2.071(44) |
| A3+ $C_{ab}$ | 0.0400/(1,-1,0) | 0.5274(94) | 0.430(49) | 0.555(36) | 0.529(53) | 0.483(16) | 0.489(71) |
| A5+ Oc | 0.0566/(0,1,0) | -1.8557(62) | -1.886(29) | -2.029(21) | -2.091(26) | -2.089(10) | -2.211(35) |
| A5+ $O_{ab}$ | 0.0308/(0,0,1) | 2.1612(63) | 2.238(22) | 2.228(16) | 2.338(18) | 2.3157(90) | 2.476(25) |
| A5+ $C_{ab}$ | 0.0435(0,0,1) | -0.6488(91) | -0.603(32) | -0.690(25) | -0.718(28) | -0.754(12) | -0.740(40) |
| A5+ $C_c$ | 0.0800/(0,1,0) | -0.4463(91) | -0.511(44) | -0.512(32) | -0.601(35) | -0.575(13) | -0.553(56) |
| A5+ $N_{DMA}$ | 0.0800/(0,1,0) | 0.8357(80) | 0.855(38) | 0.770(26) | 0.728(31) | 0.703(13) | 0.681(48) |
| A5+ $C_{DMA}$ | 0.0566/(0,1,0) | 0.531(10) | 0.517(57) | 0.579(37) | 0.591(47) | 0.635(18) | 0.652(67) |
| $R_F[I \geq 3\sigma]$ % | - | 3.64 | 6.53 | 5.31 | 4.90 | 4.99 | 6.01 |

***Table S5.*** Mode amplitudes refined as function of pressure for the triclinic *P*-1 γ-phase from single crystal x-ray data.

| Mode | | Normalization factor/direction | 7.15 GPa | 9.10 GPa |
|---|---|---|---|---|
| Γ1+ | $O_c$ | 0.03080/(0,0,1) | 0.784(28) | 1.081(76) |
| Γ1+ | $O_{ab}$ | 0.02000/(1,1,0) | 0.611(84) | 0.364(29) |
| Γ1+ | $C_{DMA}$ | 0.03080/(0,0,1) | -0.312(53) | 0.01(11) |
| Γ2+ | $O_{ab}$ | 0.02000/(1,1,0) | -1.044(85) | -0.645(30) |
| Γ3+ | $O_{ab}$ | 0.02000/(1,-1,0) | 1.293(75) | 1.325(33) |
| Γ4+ | $O_{ab}$ | 0.02000/(1,1,0) | -1.490(73) | -1.281(32) |
| Γ5+ | $O_c$ | 0.02830/(1,-1,0) | 0.823(98) | 0.920(31) |
| Γ5+ | $O_c$ | 0.02830/(1,-1,0) | 1.826(40) | 2.054(33) |
| Γ5+ | $O_{ab}$ | 0.03080/(0,0,1) | 0.914(32) | 0.842(82) |
| Γ5+ | $O_{ab}$ | 0.03080/(0,0,1) | -0.084(29) | -0.165(59) |
| Γ5+ | $C_{DMA}$ | 0.02830/(1,-1,0) | 1.23(17) | 1.704(54) |
| Γ5+ | $C_{DMA}$ | 0.02830/(1,1,0) | -2.963(76) | -2.662(56) |
| M2- | $N_{DMA}$ | 0.04350/(0,0,1) | -0.836(42) | -1.084(89) |
| M2- | $C_{DMA}$ | 0.03080/(0,0,1) | 0.303(51) | 0.39(11) |
| M3- | Cu | 0.04350/(0,0,1) | -0.331(05) | -0.46671(80) |
| M3- | $O_c$ | 0.03080/(0,0,1) | -0.462(36) | -0.33043(56) |
| M3- | $O_{ab}$ | 0.02180/(0,0,1) | -0.594(33) | -0.98331(40) |
| M3- | $C_c$ | 0.04350/(0,0,1) | -0.115(51) | -0.46671(80) |
| M4- | $O_{ab}$ | 0.02180/(0,0,1) | -0.070(36) | 0.16(10) |
| M5- | Cu | 0.05660/(1,0,0) | -0.062(20) | -0.164(10) |
| M5- | Cu | 0.05660/(0,1,0) | -0.036(11) | -0.0755(80) |
| M5- | $O_c$ | 0.124268/(1,0,0) | 0.01(12) | -0.286(33) |
| M5- | $O_c$ | 0.04000/(0,1,0) | -0.017(67) | -0.307(36) |
| M5- | $O_{ab}$ | 0.02000/(1,-1,0) | -0.192(96) | -0.217(37) |
| M5- | $O_{ab}$ | 0.02000/(1,1,0) | 0.134(99) | -0.042(44) |
| M5- | $O_{ab}$ | 0.02000/(1,1,0) | 0.389(96) | 0.571(37) |

| | | | | |
|---|---|---|---|---|
| M5- | $O_{ab}$ | 0.02000/(1,-1,0) | 0.345(96) | 0.034(48) |
| M5- | $C_c$ | 0.05660/(1,0,0) | 0.17(16) | -0.163(51) |
| M5- | $C_c$ | 0.05660/(0,1,0) | -0.491(96) | -0.635(53) |
| M5- | $N_{DMA}$ | 0.05660/(1,0,0) | -0.92(14) | -0.962(43) |
| M5- | $N_{DMA}$ | 0.05660/(0,1,0) | 0.352(83) | 0.291(42) |
| M5- | $C_{DMA}$ | 0.04000/(1,0,0) | 1.34(15) | 1.254(57) |
| M5- | $C_{DMA}$ | 0.04000/(0,1,0) | 0.751(85) | 0.942(44) |
| A1+ | $O_c$ | 0.03080/(0,0,1) | -0.280(30) | -0.224(74) |
| A1+ | $O_{ab}$ | 0.02000/(1,1,0) | 0.295(82) | 0.249(34) |
| A1+ | $C_{ab}$ | 0.02830/(1,1,0) | -0.23(15) | 0.548(63) |
| A1+ | $C_c$ | 0.04350/(0,0,1) | -0.852(49) | -0.81(13) |
| A2+ | $O_{ab}$ | 0.02000/(1,-1,0) | -0.294(77) | -0.195(35) |
| A2+ | $C_{ab}$ | 0.02830/(1,-1,0) | -0.32(15) | 0.647(62) |
| A3+ | $O_{ab}$ | 0.02000/(1,1,0) | 3.013(82) | 3.179(33) |
| A3+ | $C_{ab}$ | 0.02830(1,1,0) | -1.45(13) | -2.056(59) |
| A4+ | $O_{ab}$ | 0.02000/(1,1,0) | -0.144(82) | -0.342(34) |
| A4+ | $C_{ab}$ | 0.02830/(1,1,0) | -0.84(14) | -1.429(58) |
| A4+ | $N_{DMA}$ | 0.04350/(0,0,1) | -0.956(40) | -1.422(99) |
| A4+ | $C_{DMA}$ | 0.03080/(0,0,1) | 0.828(50) | 1.02(12) |
| A5+ | $O_c$ | 0.04000/(1,0,0) | -1.442(88) | -1.312(36) |
| A5+ | $O_c$ | 0.04000/(0,1,0) | -1.780(51) | -1.825(31) |
| A5+ | $O_{ab}$ | 0.02180/(0,0,1) | 1.047(32) | 1.094(79) |
| A5+ | $O_{ab}$ | 0.02180/(0,0,1) | 1.593(27) | 1.317(71) |
| A5+ | $C_{ab}$ | 0.03080/(0,0,1) | -0.787(59) | -1.18(13) |
| A5+ | $C_{ab}$ | 0.03080/(0,0,1) | 0.128(52) | 0.77(11) |
| A5+ | $C_c$ | 0.05660/(1,0,0) | -2.57(15) | -2.044(67) |
| A5+ | $C_c$ | 0.05660/(0,1,0) | -0.534(94) | -0.890(49) |
| A5+ | $N_{DMA}$ | 0.05660/(1,0,0) | 0.78(13) | 0.585(52) |
| A5+ | $N_{DMA}$ | 0.05660/(0,1,0) | 0.742(73) | 0.788(38) |
| A5+ | $C_{DMA}$ | 0.04000/(1,0,0) | -1.09(17) | -0.729(65) |
| A5+ | $C_{DMA}$ | 0.04000/(0,1,0) | -0.93(10) | -0.615(51) |
| Z3- | $C_u$ | 0.04350/(0,0,1) | 0.001(10) | 0.018(31) |
| Z3- | $O_c$ | 0.03080/(0,0,1) | 0.038(30) | 0.13(12) |
| Z3- | $O_{ab}$ | 0.02180/(0,0,1) | 0.008(31) | 0.026(85) |
| Z3- | $C_{ab}$ | 0.03080/(0,0,1) | 0.229(52) | 0.18(14) |
| Z3- | $C_{DMA}$ | 0.03080/(0,0,1) | 0.070(50) | 0.13(11) |
| Z4- | $O_{ab}$ | 0.02180/(0,0,1) | -0.240(31) | -0.350(92) |
| Z4- | $C_{ab}$ | 0.03080/(0,0,1) | -0.067(54) | -0.05(15) |
| Z5- | Cu | 0.05660/(1,0,0) | 0.090(40) | 0.021(15) |
| Z5- | Cu | 0.05660/(0,1,0) | 0.033(22) | -0.041(10) |
| Z5- | $O_c$ | 0.04000/(1,0,0) | -0.04(10) | 0.140(66) |
| Z5- | $O_c$ | 0.04000/(0,1,0) | 0.007(64) | 0.003(44) |
| Z5- | $O_{ab}$ | 0.02000/(1,1,0) | -0.046(95) | -0.136(44) |
| Z5- | $O_{ab}$ | 0.02000/(1,-1,0) | 0.209(97) | 0.088(49) |
| Z5- | $O_{ab}$ | 0.02000/(1,-1,0) | 0.424(83) | 0.379(40) |
| Z5- | $O_{ab}$ | 0.02000/(1,1,0) | 0.145(84) | -0.034(45) |
| Z5- | $C_{ab}$ | 0.02830(1,1,0) | 0.83(13) | 0.599(68) |
| Z5- | $C_{ab}$ | 0.02830(1,-1,0) | -0.36(14) | -0.256(70) |
| Z5- | $C_{ab}$ | 0.02830(1,-1,0) | -1.48(15) | -0.174(76) |
| Z5- | $C_{ab}$ | 0.02830(1,1,0) | -1.32(16) | -0.098(75) |
| Z5- | $C_{DMA}$ | 0.04000/(1,0,0) | 0.17(16) | -0.060(60) |
| Z5- | $C_{DMA}$ | 0.04000/(0,1,0) | -0.033(97) | 0.023(51) |
| $R_F[I \geq 3\sigma]$ % | | - | 8.98 | 5.56 |

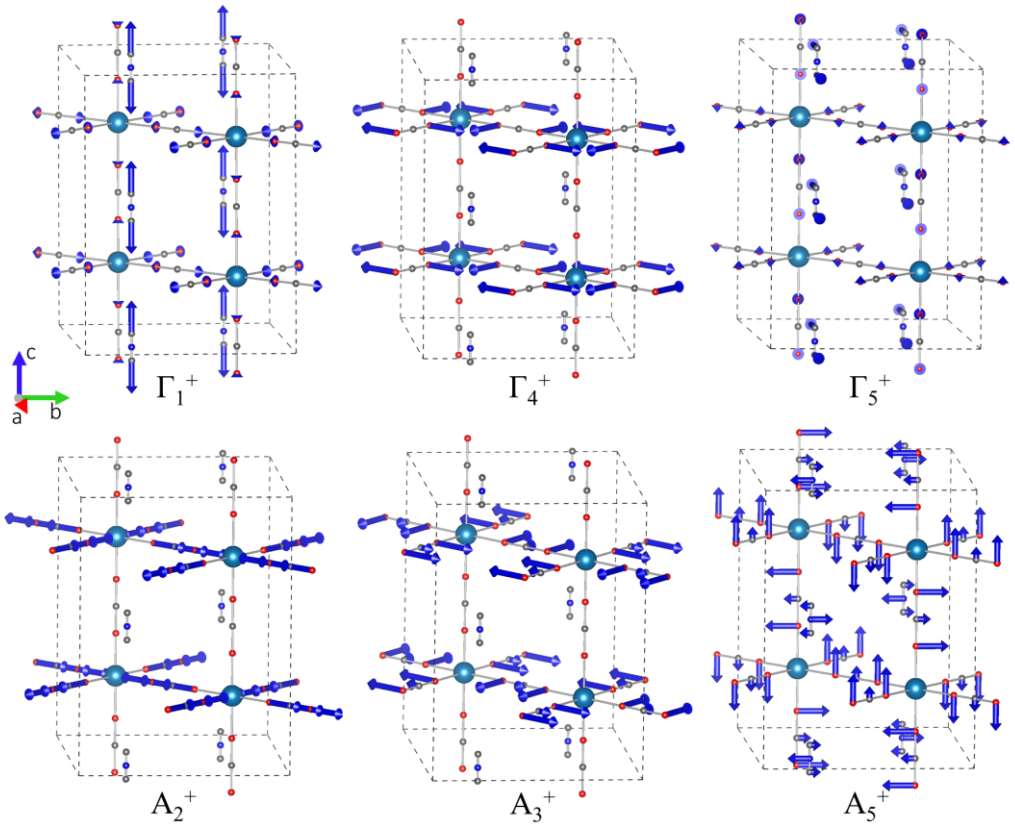
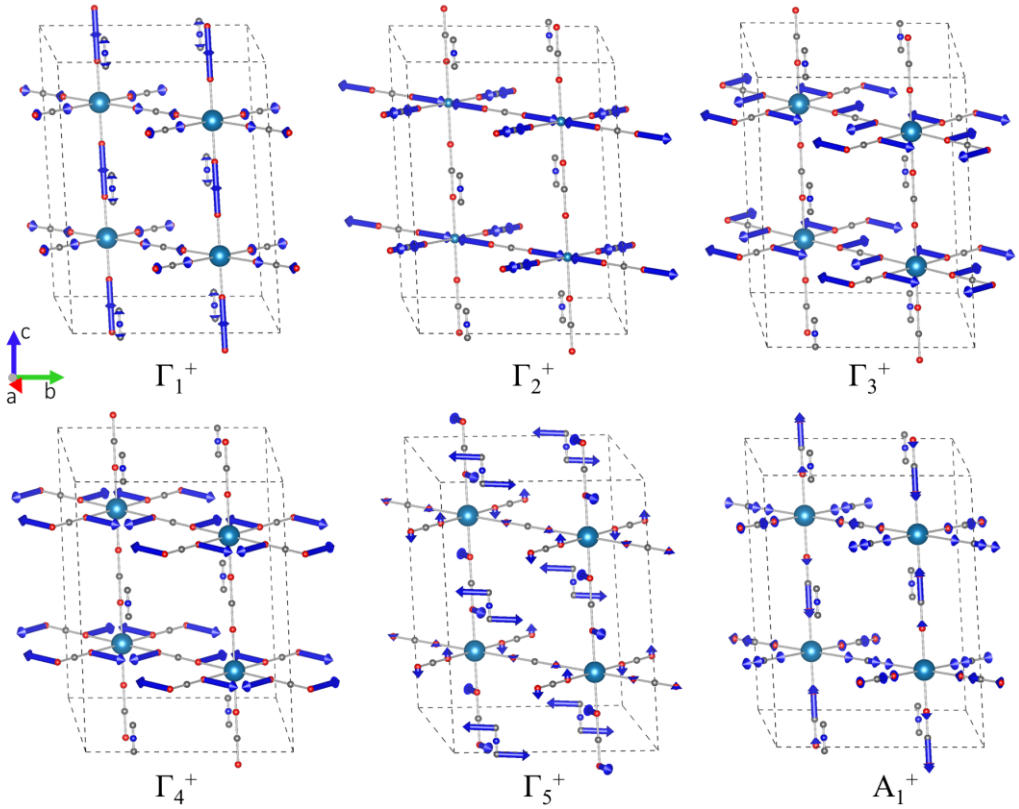



***Figure S5.*** Representation of the active irreducible representation in the monoclinic *I*2/a α-phase of $[(CH_3)_2NH_2]Cu(HCOO)_3$. H atoms were omitted from the analysis.



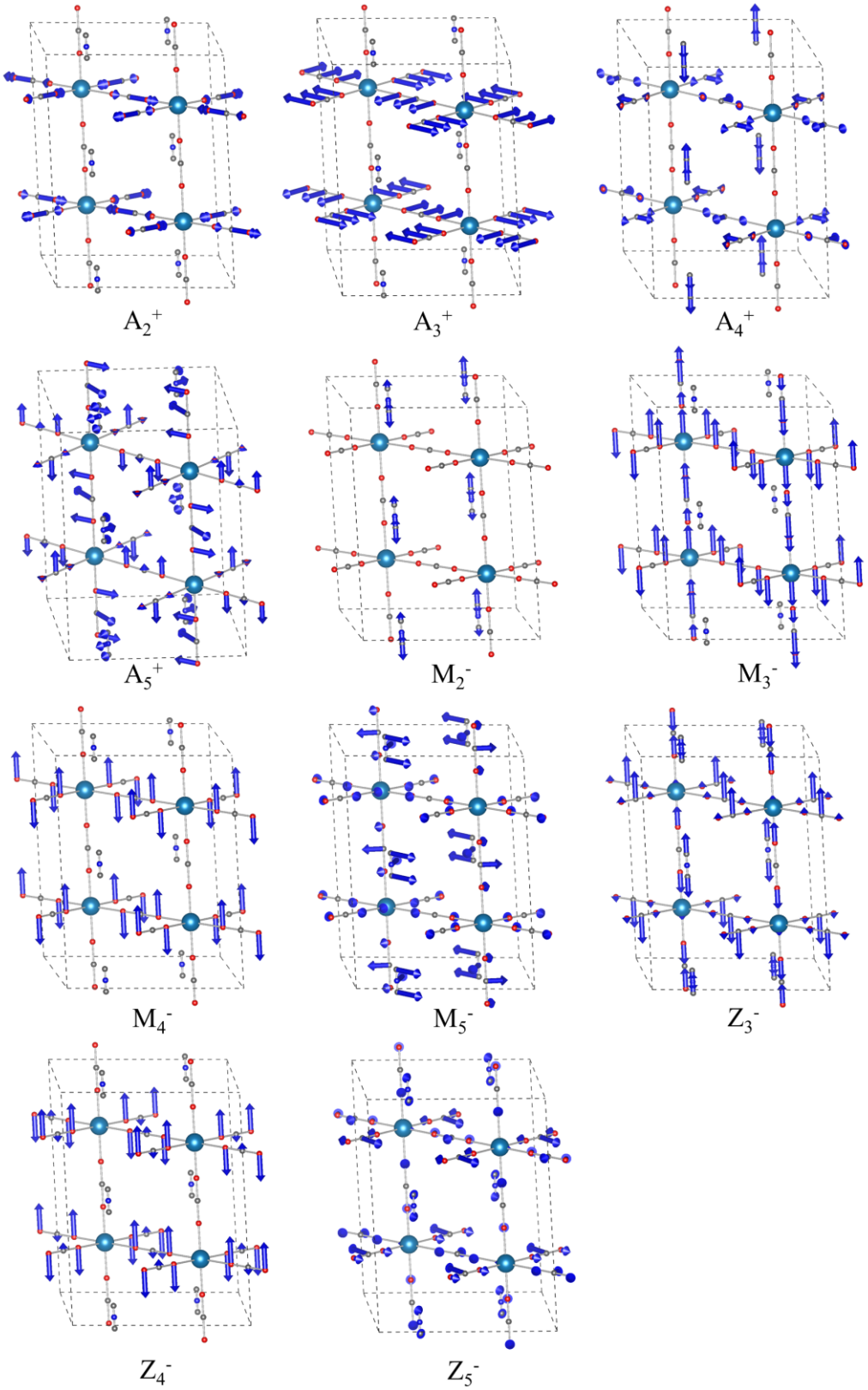



***Figure S6.*** Representation of the active irreducible representation in the triclinic *P*-1 γ-phase of $[(CH_3)_2NH_2]Cu(HCOO)_3$. H atoms were omitted from the analysis.

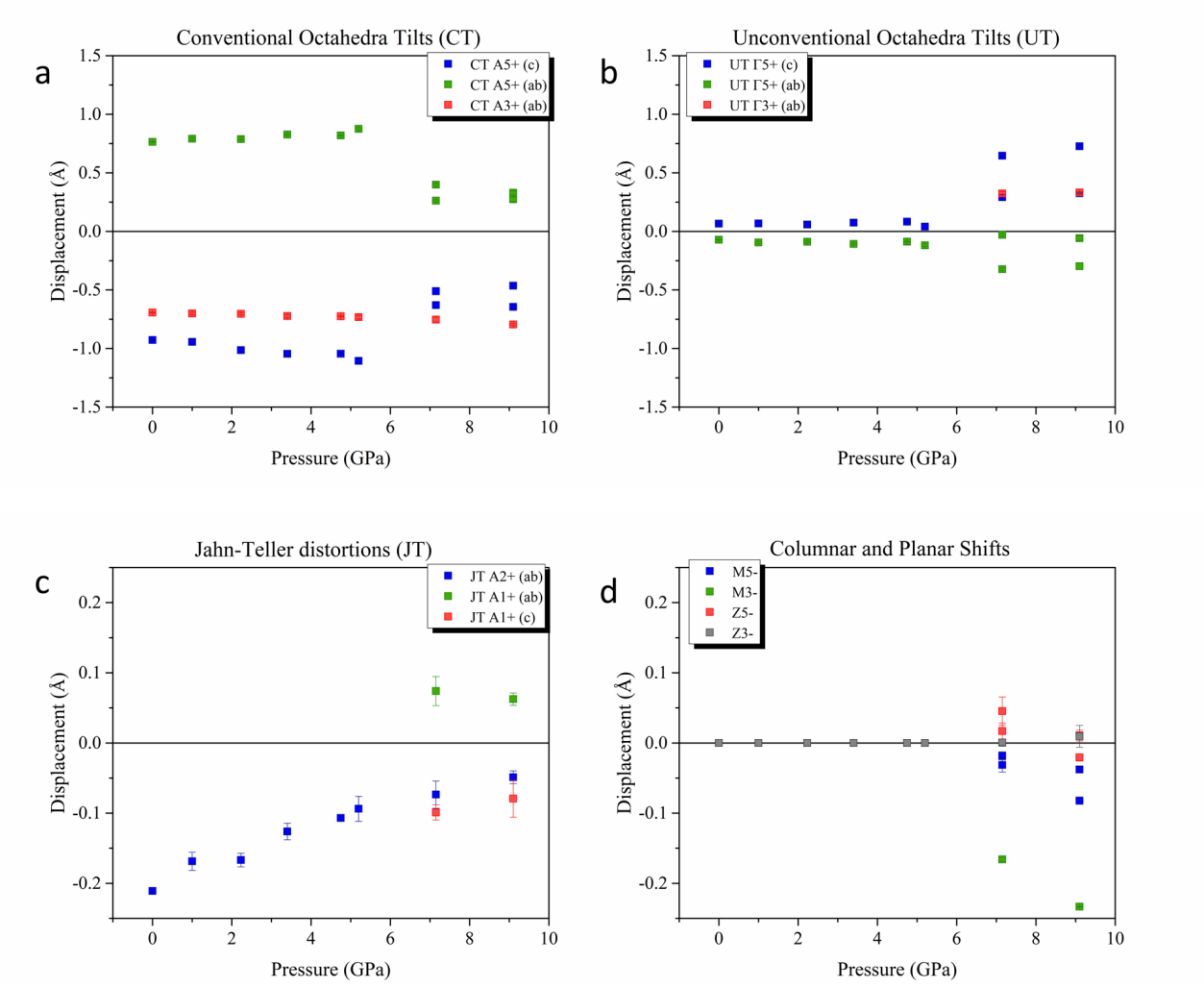



***Figure S7.*** Pressure dependence of the displacement of (a) conventional and (b) unconventional octahedra tilts, (c) Jahn-Teller distortions and (d) Columnar and planar shifts of framework.