The coordination chemistry of tartronic acid with copper: magnetic studies of a quasi-equilateral tricopper triangle.

Gabriel Pascu,[a] Claire Deville,[a] Sarah E. Clifford[a,] Laure Guenée,[b] Céline Besnard,[b] Karl W. Krämer,[c] Shi-Xia Liu,[c] Silvio Decurtins,[c] Floriana Tuna,[d] Eric J. L. McInnes,[d] Richard E. P. Winpenny[d] and Alan F. Williams*[a]

Supplementary material

Figure S1 Potentiometric titration curves for copper(II) with different copper ligand ratios

Figure S2 Plot of $\chi_m(T)$ for $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$.

Figure S3 Plot of $1/\chi_m(T)$ for $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$; the solid line represents a Curie-Weiss fit in the temperature range 270-120 K.

Figure S4 K-band (top) and Q-band (bottom) EPR spectra of polycrystalline $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$ at 4 K, and simulations (lower spectra) as described in the main text.

Figure S5 Ortep plot of $[Co(NH_3)_6][Cu(1\text{-}2H)_2Cl(OH_2)]$.

Table S1 Selected bond distances and angles for $[Co(NH_3)_6][Cu(1\text{-}2H)_2Cl(OH_2)]$.

Table S2 Hydrogen Bonds for $[Co(NH_3)_6][Cu(1\text{-}2H)_2Cl(OH_2)]$.

Figure S6. Ortep plot of the anion $[Cu_3(1\text{-}3H)_3]^{3-}$.

Table S3. Selected Bond lengths [Å] and angles [°] for the anion $[Cu_3(1\text{-}3H)_3]^{3-}$.

Table S4. Hydrogen bonds for $Rb_3[Cu_3(1\text{-}3H)_3].5H_2O$. [Å and °].

Figure S7. Ortep plot of one half of the centrosymmetric anion $[Cu_6(1\text{-}3H)_2(C_6O_{10})]^{6-}$.

Table S5. Selected Bond lengths [Å] and angles [°] for the anion $[Cu_6(1\text{-}3H)_2(C_6O_{10})]^{6-}$.

Table S6. Hydrogen-bond geometry (Å, °) for $Rb_6[\{Cu_3(1\text{-}3H)_2\}_2(C_6O_{10})].10H_2O$.

Figure S8. Juxtaposition of the structures of $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$ and $Na_3[Cu_3(malate)_3(H_2O)].8H_2O$

Figure S1

Potentiometric titration curves for copper(II) with different copper ligand ratios

$M + L \leftrightarrow ML$

$M + L \leftrightarrow MLH_{-1} + H$

$M + 2L \leftrightarrow ML_2$

$\log \beta_{11} = 5.91$ (8)	$\log K_{11} = 5.91$ (8)
$\log \beta_{11\text{-}1} = 1.62$ (8)	$\log K_{11\text{-}1} = 15.62$ (8)
$\log \beta_{12} = 8.72$ (11)	$\log K_{12} = 2.82$ (14)

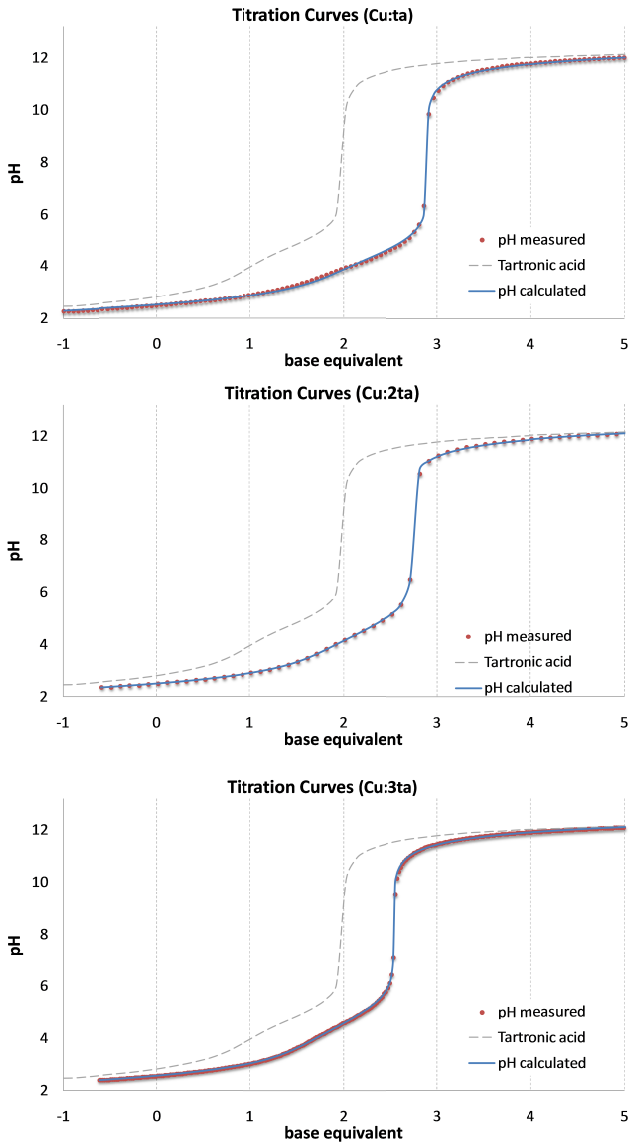


Figure S2. Plot of $\chi_m(T)$ for $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$.

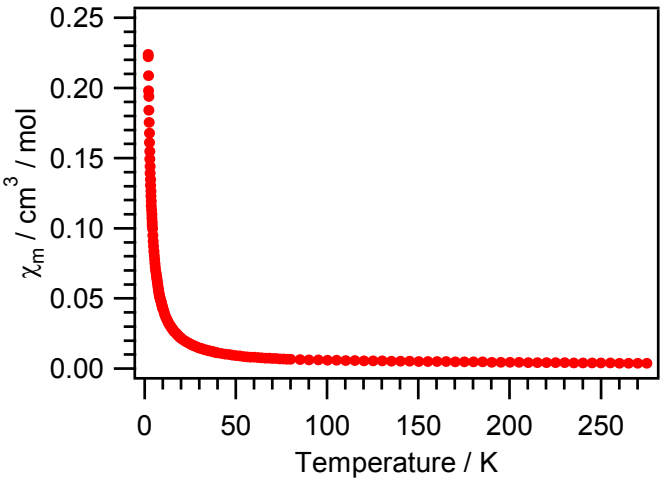


Figure S3. Plot of $1/\chi_m(T)$ for $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$; the solid line represents a Curie-Weiss fit in the temperature range 270-120 K.

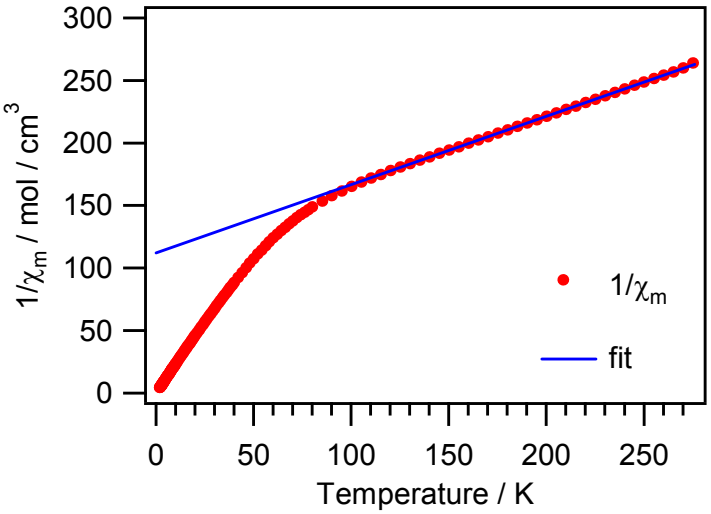
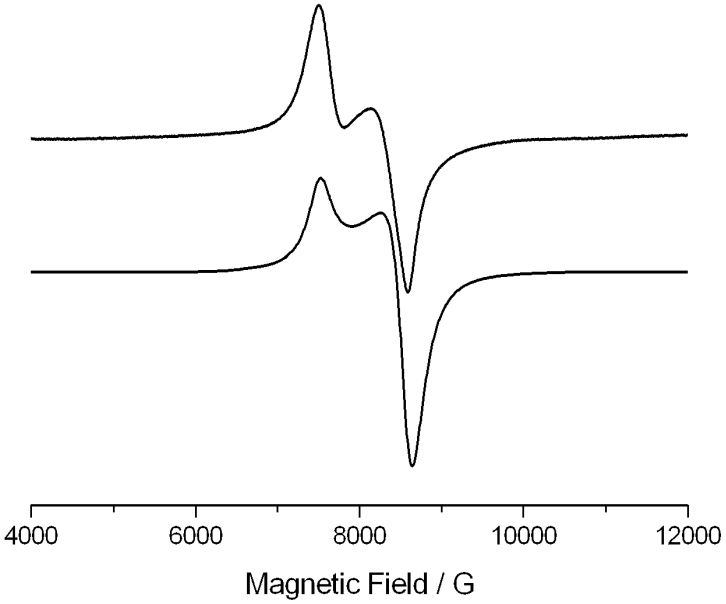


Figure S4. K-band (top) and Q-band (bottom) EPR spectra of polycrystalline $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$ at 4 K, and simulations (lower spectra) as described in the main text.



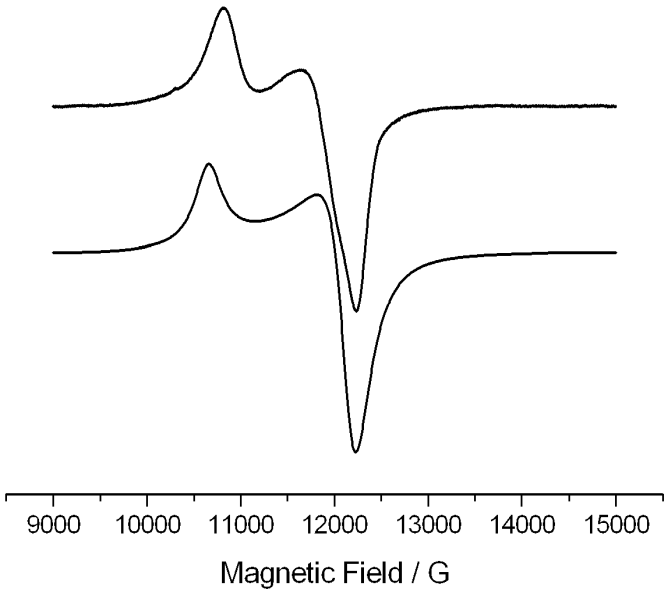


Figure S5. Ortep plot of $[Co(NH_3)_6][Cu(1\text{-}2H)_2Cl]$.

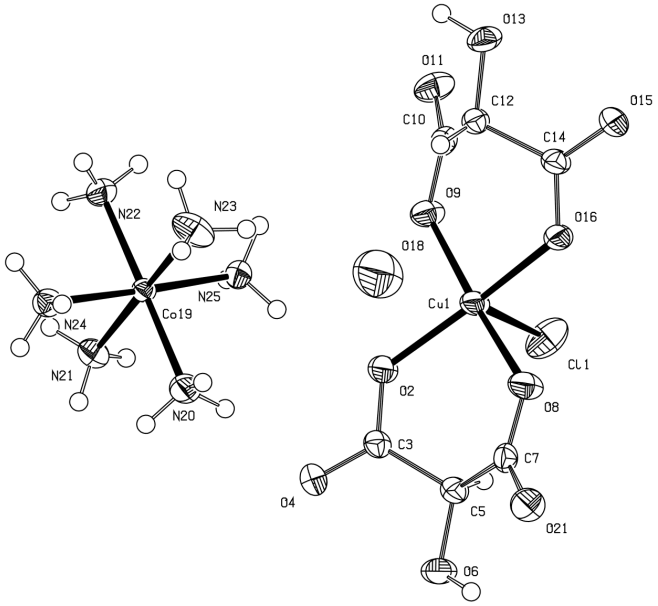


Table S1 Selected bond distances and angles for $[Co(NH_3)_6][Cu(1\text{-}2H)_2Cl(OH_2)]$.

Cu1—O2	1.939 (2)	Cu1—O9	1.967 (2)
Cu1—O8	1.961 (2)	Cu1—O16	1.941 (2)
Cu1—Cl1	2.7899 (12)	O9—C10	1.270 (4)
O2—C3	1.275 (4)	C10—O11	1.244 (4)
C3—O4	1.232 (4)	C10—C12	1.531 (4)
C3—C5	1.523 (4)	C12—O13	1.411 (4)
C5—O6	1.399 (4)	C12—C14	1.531 (4)
C5—C7	1.541 (4)	C12—H12	0.935
C5—H22	0.942	O13—H8	0.913
O6—H18	0.862	C14—O15	1.229 (4)
C7—O8	1.265 (4)	C14—O16	1.284 (4)
C7—O21	1.231 (4)		
O2—Cu1—O8	92.26 (10)	O2—Cu1—Cl1	94.08 (9)
O2—Cu1—O9	91.80 (10)	O8—Cu1—Cl1	98.34 (9)
O8—Cu1—O9	174.72 (10)	O9—Cu1—Cl1	84.73 (8)
O2—Cu1—O16	167.70 (12)	O16—Cu1—Cl1	97.84 (8)
O8—Cu1—O16	83.09 (10)	O9—Cu1—O16	92.25 (10)
Cu1—O2—C3	127.2 (2)	Cu1—O9—C10	124.3 (2)
O2—C3—O4	122.7 (3)	O9—C10—O11	123.9 (3)
O2—C3—C5	117.2 (3)	O9—C10—C12	116.9 (3)
O4—C3—C5	120.1 (3)	O11—C10—C12	119.3 (3)
C3—C5—O6	110.5 (3)	O6—C5—H22	111.2
C3—C5—C7	112.6 (3)	C7—C5—H22	105.5

O6—C5—C7	111.5 (3)	C5—O6—H18	110.4
C3—C5—H22	105.3	C5—C7—O8	116.9 (3)
C5—C7—O21	118.0 (3)	C10—C12—O13	113.8 (3)
O8—C7—O21	125.0 (3)	C10—C12—C14	110.0 (3)
C7—O8—Cu1	126.4 (2)	O13—C12—C14	108.7 (3)
C10—C12—H12	105.8	C12—C14—O15	119.9 (3)
O13—C12—H12	112.1	C12—C14—O16	117.2 (3)
C14—C12—H12	106.2	O15—C14—O16	122.8 (3)
C12—O13—H8	108.5	C14—O16—Cu1	125.9 (2)

Table S2 Hydrogen Bonds for $[Co(NH_3)_6][Cu(1\text{-}2H)_2Cl(OH_2)]$.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H8···O16^{i}	0.91	2.18	3.002 (5)	149
O6—H18···O2^{ii}	0.86	2.58	3.099 (5)	120
N20—H26···O4^{iii}	0.90	2.04	2.904 (5)	163
N20—H27···O4	0.90	2.08	2.964 (5)	165
N24—H29···O8^{iv}	0.88	2.49	3.242 (5)	143
N24—H29···O13^{v}	0.88	2.56	3.271 (5)	139
N24—H30···O9^{vi}	0.89	2.16	3.046 (5)	170
N24—H31···O6^{iii}	0.90	2.07	2.915 (5)	155
N21—H33···O4^{iii}	0.89	2.29	3.121 (5)	157
N21—H34···O21^{vii}	0.91	2.16	2.935 (5)	143
N22—H37···O13^{i}	0.90	2.21	3.103 (5)	175
N22—H39···O11^{vi}	0.90	2.06	2.948 (5)	168
N25—H41···O21^{vii}	0.90	2.26	3.135 (5)	164
N25—H42···O2	0.89	2.07	2.942 (5)	166
N25—H43···O15^{i}	0.91	2.12	2.961 (5)	155
N23—H46···O16^{iv}	0.89	2.27	3.113 (5)	158
N23—H47···O18	0.90	2.44	3.257 (5)	151

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) −*x*, −*y*+1, −*z*+1; (iv) *x*, −*y*+1/2, *z*+1/2; (v) −*x*+1, −*y*+1, −*z*+1; (vi) *x*, −*y*+3/2, *z*+1/2; (vii) *x*, *y*+1, *z*.

Figure S6. Ortep plot of the anion $[Cu_3(1\text{-}3H)_3]^{3-}$.

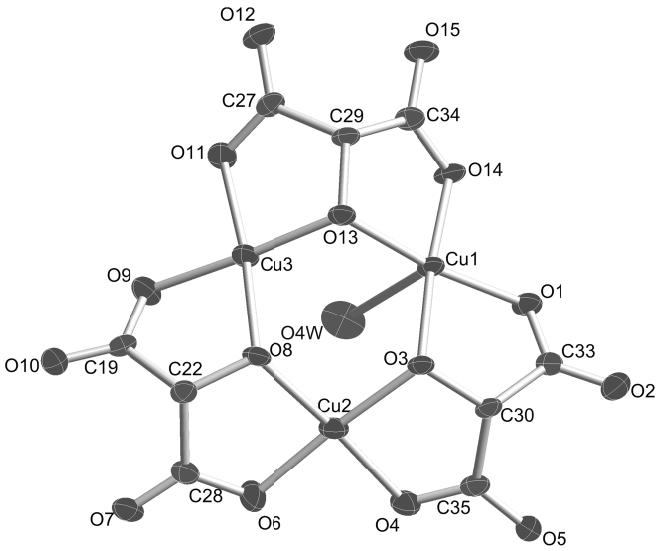


Table S3. Selected Bond lengths [Å] and angles [°] for the anion $[Cu_3(1\text{-}3H)_3]^{3-}$.

Cu(1)-O(1)	1.925(3)	Cu(2)-O(3)	1.923(3)
Cu(1)-O(13)	1.934(3)	Cu(2)-O(8)	1.923(3)
Cu(1)-O(14)	1.946(4)	Cu(3)-O(13)	1.919(3)
Cu(1)-O(3)	1.950(3)	Cu(3)-O(9)	1.926(4)
Cu(2)-O(6)	1.912(4)	Cu(3)-O(11)	1.928(4)
Cu(2)-O(4)	1.914(4)	Cu(3)-O(8)	1.951(4)
O(1)-C(33)	1.279(6)	O(12)-C(27)	1.219(6)
O(2)-C(33)	1.230(6)	O(13)-C(29)	1.420(6)
O(3)-C(30)	1.414(5)	O(14)-C(34)	1.273(6)
O(4)-C(35)	1.277(7)	O(15)-C(34)	1.236(7)
O(5)-C(35)	1.234(6)	C(19)-C(22)	1.541(6)
O(6)-C(28)	1.295(7)	C(22)-C(28)	1.535(7)
O(7)-C(28)	1.208(7)	C(27)-C(29)	1.540(7)
O(8)-C(22)	1.422(6)	C(29)-C(34)	1.545(7)
O(9)-C(19)	1.271(6)	C(30)-C(33)	1.527(7)
O(10)-C(19)	1.234(6)	C(30)-C(35)	1.543(7)
O(11)-C(27)	1.293(7)		

O(1)-Cu(1)-O(13)	171.71(15)	O(6)-Cu(2)-O(8)	85.43(16)
O(1)-Cu(1)-O(14)	88.19(15)	O(4)-Cu(2)-O(8)	175.37(15)
O(13)-Cu(1)-O(14)	86.13(15)	O(3)-Cu(2)-O(8)	98.25(14)
O(1)-Cu(1)-O(3)	85.11(15)	O(13)-Cu(3)-O(9)	176.22(16)

O(13)-Cu(1)-O(3)	100.82(14)	O(13)-Cu(3)-O(11)	86.46(15)
O(14)-Cu(1)-O(3)	172.77(14)	O(9)-Cu(3)-O(11)	89.91(16)
O(6)-Cu(2)-O(4)	90.31(17)	O(13)-Cu(3)-O(8)	98.29(15)
O(6)-Cu(2)-O(3)	175.89(18)	O(9)-Cu(3)-O(8)	85.43(16)
O(4)-Cu(2)-O(3)	86.07(15)	O(11)-Cu(3)-O(8)	172.89(16)
C(33)-O(1)-Cu(1)	113.7(3)	Cu(2)-O(8)-Cu(3)	124.52(18)
C(30)-O(3)-Cu(2)	110.7(3)	C(19)-O(9)-Cu(3)	112.4(3)
C(30)-O(3)-Cu(1)	111.1(3)	C(27)-O(11)-Cu(3)	114.0(3)
Cu(2)-O(3)-Cu(1)	119.92(18)	C(29)-O(13)-Cu(3)	110.8(3)
C(35)-O(4)-Cu(2)	115.3(3)	C(29)-O(13)-Cu(1)	110.1(3)
C(28)-O(6)-Cu(2)	115.9(3)	Cu(3)-O(13)-Cu(1)	117.08(17)
C(22)-O(8)-Cu(2)	111.5(3)	C(34)-O(14)-Cu(1)	113.0(3)
C(22)-O(8)-Cu(3)	109.3(3)	O(13)-C(29)-C(34)	111.9(4)
O(10)-C(19)-O(9)	124.3(5)	C(27)-C(29)-C(34)	109.2(4)
O(10)-C(19)-C(22)	120.0(4)	O(3)-C(30)-C(33)	111.5(4)
O(9)-C(19)-C(22)	115.6(4)	O(3)-C(30)-C(35)	112.0(4)
O(8)-C(22)-C(28)	111.8(4)	C(33)-C(30)-C(35)	110.4(4)
O(8)-C(22)-C(19)	111.7(4)	O(2)-C(33)-O(1)	124.6(5)
C(28)-C(22)-C(19)	108.7(4)	O(2)-C(33)-C(30)	119.6(5)
O(12)-C(27)-O(11)	124.9(5)	O(1)-C(33)-C(30)	115.9(4)
O(12)-C(27)-C(29)	121.0(5)	O(15)-C(34)-O(14)	123.7(5)
O(11)-C(27)-C(29)	114.1(4)	O(15)-C(34)-C(29)	119.6(5)
O(7)-C(28)-O(6)	123.8(5)	O(14)-C(34)-C(29)	116.6(4)
O(7)-C(28)-C(22)	122.0(5)	O(5)-C(35)-O(4)	123.8(5)
O(6)-C(28)-C(22)	114.2(4)	O(5)-C(35)-C(30)	121.4(5)
O(13)-C(29)-C(27)	112.7(4)	O(4)-C(35)-C(30)	114.7(4)

Table S4. Hydrogen bonds for $Rb_3[Cu_3(1\text{-}3H)_3].5H_2O$. [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(15)#3	0.74	2.10	2.834(6)	173.7
O(1W)-H(1WB)...O(10)#11	0.94	2.00	2.870(6)	154.9
O(1W)-H(1WB)...O(7)#11	0.94	2.47	3.030(5)	118.6
O(2W)-H(2WA)...O(1W)	0.76	2.15	2.873(6)	159.1
O(2W)-H(2WB)...O(10)#5	0.78	2.01	2.791(6)	174.6
O(3W)-H(3WA)...O(4W)#9	0.88	2.26	2.832(8)	122.4
O(3W)-H(3WB)...O(2)#6	0.85	1.87	2.604(7)	144.2

O(16A)-H(16A)...O(4)#6	0.83	1.97	2.797(10)	174.3
O(16A)-H(16B)...O(6)#4	0.87	1.95	2.823(11)	176.2
O(16A)-H(16B)...O(7)#4	0.87	2.69	3.309(11)	128.6
O(16B)-H(16C)...O(6)#4	1.00	1.79	2.780(11)	175.8
O(16B)-H(16D)...O(4)#6	0.99	1.86	2.845(10)	169.9
O(4W)-H(4WA)...O(3W)	0.95	1.72	2.649(8)	163.7
O(4W)-H(4WB)...O(16A)#10	0.85	1.90	2.606(11)	139.0
O(4W)-H(4WB)...O(16B)#10	0.85	2.13	2.644(12)	118.3

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 -x,y+1/2,-z+3/2 #3 -x+1,y+1/2,-z+3/2

#4 x+1,y-1,z #5 x+1,y,z #6 -x+1,-y+1,-z+1

#7 -x+1,y-1/2,-z+3/2 #8 x,y-1,z #9 -x,-y+1,-z+1

#10 x-1,y,z #11 -x,y-1/2,-z+3/2 #12 x-1,y+1,z

Figure S7. Ortep plot of one half of the centrosymmetric anion $[Cu_6(1\text{-}3H)_2(C_6O_{10})]^{6-}$.

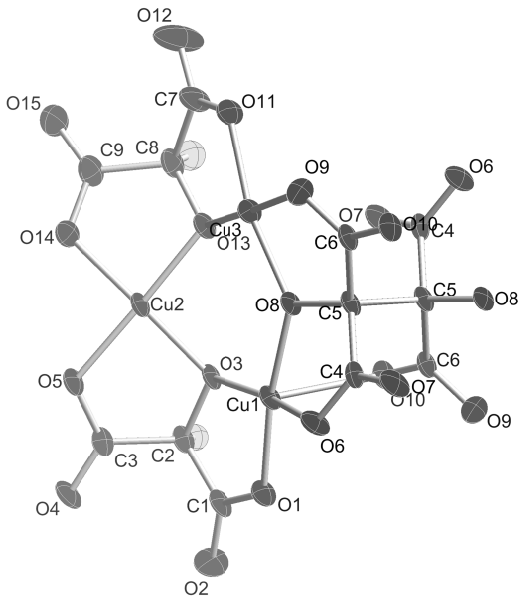


Table S5. Selected Bond lengths [Å] and angles [°] for the anion $[Cu_6(1\text{-}3H)_2(C_6O_{10})]^{6-}$.

Cu1—O1	1.914 (4)	O6—C4	1.278 (8)
Cu1—O8	1.921 (4)	O7—C4	1.227 (8)
Cu1—O3	1.929 (4)	O8—C5	1.401 (7)

Cu1—O6	1.947 (5)	O9—C6	1.281 (8)
Cu2—O3	1.917 (4)	O10—C6	1.239 (8)
Cu2—O13	1.930 (4)	O11—C7	1.284 (9)
Cu2—O14	1.935 (5)	O12—C7	1.244 (9)
Cu2—O5	1.941 (4)	O13—C8	1.408 (8)
Cu3—O8	1.917 (4)	O14—C9	1.277 (8)
Cu3—O9	1.919 (5)	O15—C9	1.224 (9)
Cu3—O13	1.922 (4)	C1—C2	1.522 (9)
Cu3—O11	1.933 (5)	C2—C3	1.526 (8)
O1—C1	1.274 (8)	C4—C5	1.558 (8)
O2—C1	1.241 (8)	C5—C6	1.544 (8)
O3—C2	1.421 (7)	C5—C5^{i}	1.636 (11)
O4—C3	1.230 (8)	C7—C8	1.533 (10)
O5—C3	1.299 (8)	C8—C9	1.547 (9)

O3—Cu2—O5	85.12 (18)	O3—C2—C1	110.0 (5)
O13—Cu2—O5	178.46 (19)	O3—C2—C3	111.5 (5)
O14—Cu2—O5	92.96 (19)	C1—C2—C3	114.5 (5)
O8—Cu3—O9	82.99 (18)	O4—C3—O5	122.8 (6)
O8—Cu3—O13	98.77 (18)	O4—C3—C2	122.5 (6)
O9—Cu3—O13	176.0 (2)	O5—C3—C2	114.6 (5)
O8—Cu3—O11	167.7 (2)	O7—C4—O6	124.9 (6)
O9—Cu3—O11	91.9 (2)	O7—C4—C5	121.4 (5)
O13—Cu3—O11	85.7 (2)	O6—C4—C5	113.5 (5)
C1—O1—Cu1	114.4 (4)	O8—C5—C6	108.8 (5)
C2—O3—Cu2	109.8 (3)	O8—C5—C4	109.0 (5)
C2—O3—Cu1	111.8 (4)	C6—C5—C4	114.7 (5)
Cu2—O3—Cu1	122.7 (2)	O8—C5—C5^{i}	112.0 (6)
C3—O5—Cu2	113.8 (4)	C6—C5—C5^{i}	107.2 (5)
C4—O6—Cu1	114.8 (4)	C4—C5—C5^{i}	105.1 (6)
C5—O8—Cu3	112.9 (3)	O10—C6—O9	123.0 (5)
C5—O8—Cu1	110.5 (4)	O10—C6—C5	122.5 (5)
Cu3—O8—Cu1	136.6 (2)	O9—C6—C5	114.4 (5)
C6—O9—Cu3	115.8 (4)	O12—C7—O11	123.4 (7)
C7—O11—Cu3	114.0 (4)	O12—C7—C8	120.4 (7)
C8—O13—Cu3	112.0 (4)	O11—C7—C8	116.2 (6)
C8—O13—Cu2	110.3 (4)	O13—C8—C7	111.3 (5)
Cu3—O13—Cu2	118.2 (2)	O13—C8—C9	111.4 (5)
C9—O14—Cu2	113.9 (4)	C7—C8—C9	111.9 (6)
O2—C1—O1	122.7 (7)	O15—C9—O14	124.0 (7)
O2—C1—C2	120.0 (6)	O15—C9—C8	120.4 (6)
O1—C1—C2	117.2 (5)	O14—C9—C8	115.5 (6)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+2

Table S6. Hydrogen-bond geometry (Å, °) for $Rb_6[\{Cu_3(1\text{-}3H)_2\}_2(C_6O_{10})].10H_2O$.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O7^{vi}	0.87	2.00	2.747 (8)	144
O1*W*—H1*WB*···O12^{xii}	0.87	1.86	2.726 (9)	173
O2*W*—H2*WA*···O1*W*^{iii}	0.76	2.49	2.881 (17)	114
O2*W*—H2*WB*···O3*W*^{xiii}	0.86	2.35	2.81 (2)	114

Symmetry codes: (iii) *x*+1, *y*, *z*; (vi) *x*−1, *y*, *z*; (xii) *x*−1, *y*, *z*−1; (xiii) −*x*+2, −*y*+2, −*z*+1.

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Figure S8. Juxtaposition of the structures of $Rb_3[Cu_3(1\text{-}3H)_3]\cdot 5H_2O$ (left) and $Na_3[Cu_3(malate)_3(H_2O)].8H_2O$ (right).