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Supporting Information Part 2 of 2 – Crystallography

Copper(II) complexes of *N*-propargyl cyclam ligands reveal a range of coordination modes and colours, and unexpected reactivity

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Contents

1. Single Crystal X-ray Diffraction Structure Determination

Suitable single crystal specimens were selected and attached with Exxon Paratone N oil to a short length of fibre supported on a thin piece of copper wire inserted in a copper mounting pin. The crystals were cooled to 150.0(5) Kelvin, using a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. Except where stated otherwise, data were collected using a SuperNova Dual instrument equipped with an Atlas detector and employing mirror monochromated Cu (Kα) radiation from a micro-source. Unless otherwise stated, data processing was undertaken with CrysAlis Pro[1] and a multi-scan absorption correction was applied[1] to the data. In general data were obtained using ShelXS[2] and, in all cases, extended and refined with ShelXL-2018/3.[3] Computations and image generation were undertaken with the assistance of the WinGX[4,5], ShelXle[6] and Olex2[7] user interfaces. In general, the non-hydrogen atoms were modelled with anisotropic displacement parameters and a

riding atom model with group displacement parameters was used for the hydrogen atoms. Crystallographic details are provided in Tables SX1 and SX2.

Of note, the crystallisation of [Cu(**9**)]$(ClO_4)_2$ produced five visibly distinct crystals, distinguished here with labels **9A** to **9E**, reflecting five unique structures.

Complex [Cu(6)]$(ClO_4)_2$ **($C_{13.25}H_{27}Cl_2CuN_4O_{8.25}$)**

A purple plate like crystal was mounted on a Bruker SMART 1000 CCD diffractometer employing graphite monochromated Mo Kα radiation generated from a sealed tube. Cell constants were obtained from a least squares refinement against 7,362 reflections located between 4 and 57º 2θ, and full-sphere data were collected with omega scans to 58º 2θ. The data integration and reduction were undertaken with SAINT and XPREP[8], and Gaussian and multi-scan corrections using SADABS[9–11] were applied to the data.

The structure was obtained in the space group *C*2/c(#15) using the Olex2 implementation of charge flipping.[12] In final difference maps the asymmetric unit contained residual electron density sites that have been modelled as partially occupied methanol sties disordered over two locations near a two-fold axis. The occupancy of these sites was refined and then fixed. The partially occupied methanol molecule sites were modelled with isotropic displacement parameters. A riding atom model with group displacement parameters was used for the hydrogen atoms. The hydrogen atom sites of the methanol solvate molecule could not be located; the calculated positions included in the model are cosmetic. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX1.

Complex [Cu(7)]$(ClO_4)_2$ **($C_{20}H_{35}Cl_2CuN_5O_8$)**

A blue block like crystal was selected and cell constants were obtained from a least squares refinement against 68,830 reflections located between 10 and 152º 2θ. Full sphere data were collected with ω scans to 152º 2θ. The structure was obtained in the space group $P2_1/c$(#14). The asymmetric unit contains a distorted square pyramidal macrocycle complex with an acetonitrile solvent molecule as the axial ligand, together with two perchlorate counterions. One of the perchlorate anions is axially located *trans* to the coordinated solvent, but with a metal to oxygen distance of 3.914(4)Å, and the interaction is presumably essentially ionic. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX2.

Complex [Cu(8)]$(ClO_4)_2$ **($C_{22}H_{34}Cl_2CuN_4O_{10}$)**

A translucent dark blue prismatic crystal was selected, and cell constants were obtained from a least squares refinement against 60,200 reflections located between 6 and 152º 2θ. Full sphere data were collected with ω scans to 152º 2θ. The structure was obtained in the space group $P2_1/c$(#14). The

asymmetric unit contains a distorted square pyramidal macrocycle complex with the carbonyl oxygen from the pendant methyl ester in the apical position, together with two perchlorate counterions. One of the perchlorate anions is axially located trans to the coordinated solvent, with a metal to oxygen distance of 3.649(2) Å suggesting a largely ionic interaction. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX3.

Complex 9A **($C_{22}H_{32}Cl_2CuN_4O_8$)**

A translucent light blue prism like crystal was selected, and cell constants were obtained from a least squares refinement against 28,012 reflections located between 8 and 152º 2θ. Full sphere data were collected with ω scans to 152º 2θ. The structure was obtained in the space group $P2_1/n$(#14). The asymmetric unit contains an essentially square pyramidal cyclam complex cation, with an apical perchlorato anion and a second perchlorate counterion. The coordinated anion is disordered over two slightly different orientations, with occupancies refined and then fixed at 0.6 and 0.4. The metal to coordinated oxygen distances are 2.359(9) and 2.301(17) Å. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX4. The complex cation is pseudo oligomeric, with the copper of one complex cation weakly interacting with the coordinated perchlorate of a second (Figure SX5), with metal to neighbouring perchlorate oxygen distances of approximately 3.51 Å for the major perchlorate orientation and 3.68 Å for the minor orientation.

Complex 9B **($C_{22}H_{32}Cl_2CuN_4O_8$)**

A translucent red prism like crystal was selected, and cell constants were obtained from a least squares refinement against 10,877 reflections located between 9 and 151º 2θ. Full sphere data were collected with ω scans to 152º 2θ. The structure was obtained in the space group $P2_1/c$(#14). The asymmetric unit contains half of the complex, which is centred on an inversion centre, and a perchlorate counterion. The complex is effectively octahedral, with necessarily weak axial pi-coordination from a 1,8-*N*-propargyl moiety reflected in a bond length of approximately 2.93 Å. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX6.

Complex 9C-1 and 9C-2 **($C_{22}H_{33.34}Cl_2CuN_4O_{8.67}$)**

A violet block like crystal was selected, and cell constants were obtained from a least squares refinement against 21,323 reflections located between 6 and 151º 2θ. Full sphere data were collected with ω scans to 144º 2θ. The structure was obtained in the space group $P\ \bar{1}$(#2).

Together with three perchlorate counterions and a water molecule, the asymmetric unit includes a six-coordinate macrocycle complex (**9C-1**), with weak axial pi-coordination from an *N*-propargyl moiety and an axially coordinated perchlorate counterion completing a distorted octahedral coordination sphere. The metal to perchlorate oxygen atom distance is 2.890(2) Å and the metal to

pi-bond distance is approximately 3.04 Å.

The asymmetric unit also includes half a macrocycle complex molecule located on an inversion centre that has an axially pi-coordinated *N*-propargyl residue (**9C-2**). The coordination of this complex is then effectively octahedral, with symmetrical and weak axial bonds of approximately 2.93 Å.

Olex2 generated depictions of the complex molecules with 50% displacement ellipsoids are provided in Figure SX7a and Figure SX7b.

Complex 9D **($C_{23}H_{38}Cl_2CuN_4O_{10}$)**

A dark blue blade like crystal was selected and mounted on an APEXII-FR591 diffractometer employing mirror monochromated MoKα radiation generated from a rotating anode. Cell constants were obtained from a least squares refinement against 9,990 reflections located between 5 and 57º 2θ. Full sphere data were collected with ω and ϕ scans to 61.02º 2θ. The data integration and reduction were undertaken with SAINT and XPREP.[8] A multi-scan absorption correction determined with SADABS[9–11] was applied to the data. The structure was obtained in the space group $P2_1/c$(#14) by direct methods with SIR2011.[13] Of the 38 hydrogen atoms included in the model 2 were located and modelled with isotropic displacement parameters, and a riding atom model was used for the remainder. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX8.

Complex 9E **($C_{24}H_{40}Cl_2CuN_4O_{10}$)**

A dark violet prismatic crystal was selected and mounted on an APEXII-FR591 diffractometer employing mirror monochromated MoKα radiation generated from a rotating anode. Cell constants were obtained from a least squares refinement against 9,854 reflections located between 5 and 68º 2θ. Full sphere data were collected with ω and ϕ scans to 70º 2θ. The data integration and reduction were undertaken with SAINT and XPREP.[8] A multi-scan absorption correction determined with SADABS[9,10] was applied to the data. The structure was obtained in the space group $P2_1/n$(#14) by direct methods with SIR97.[13] The asymmetric unit of the structure model contains the complex dication, together with two perchlorate counterions disordered over multiple sites and a methanol solvate molecule. Rigid bodies with isotropic displacement parameters were used to model the perchlorate counterions, with site occupancies refined and then fixed at the first decimal place. An Olex2 generated depiction of the molecule with 50% displacement ellipsoids is provided in Figure SX9.

2. Crystallographic Details

Table SX1. Crystallographic details for complexes of ligands 6, 7 and 8

	[Cu(**6**)](ClO$_4$)$_2$	[Cu(**7**)](ClO$_4$)$_2$	[Cu(**8**)](ClO$_4$)$_2$
CSD Submission Number	2012634	2012628	2012629
Refinement Model Formula	$C_{13.25}H_{27}Cl_2CuN_4O_{8.25}$	$C_{20}H_{35}Cl_2CuN_5O_8$	$C_{22}H_{34}Cl_2CuN_4O_{10}$
Model Molecular Weight	508.83	607.97	648.97
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	*C*2/c(#15)	$P2_1$/c(#14)	$P2_1$/c(#14)
a (Å)	31.689(5)	17.9502(2)	8.15300(10)
b (Å)	8.5129(12)	9.1454(2)	17.56480(10)
c (Å)	16.517(2)	16.40970(10)	19.34900(10)
β (º)	112.422(2)	106.329(2)	96.9230(10)
V (Å^3)	4118.9(10)	2585.18(7)	2750.69(4)
D_c (g cm^{-3})	1.641	1.562	1.567
Z	8	4	4
Crystal Size (mm)	0.31x0.17x0.03	0.12x0.07x0.03	0.427x0.302x0.225
Crystal Colour	purple	blue	translucent dark blue
Crystal Habit	plate	block	prism
Temperature (Kelvin)	150.0(5)	150.0(5)	150.0(5)
λ(Mo Kα, Å)	0.71073	1.5418	1.5418
μ(Mo Kα, mm^{-1})	1.370	3.569	3.444
$T_{min,max}$	0.729, 0.928	0.78912, 1.00	0.55033, 1.00
$2\theta_{max}$ (º)	57.79	151.79	152.02º
hkl range	-42 42, -11 11, -22 22	-22 22, -11 11, -20 20	-10 10, -21 21, -24 24
N	19982	66254	97600
N_{ind}	5064(R_{merge} 0.0293)	5401(R_{merge} 0.0502)	5732(R_{merge} 0.0687)
N_{obs}	4234(I > 2σ(I))	4927(I > 2σ(I))	5412(I > 2σ(I))
N_{var}	266	328	397
Residuals* *R*1(*F*), *wR*2(F^2)	0.0358, 0.0907	0.0592, 0.1397	0.0414, 0.1076
GoF(all)	1.362	1.194	1.365
Residual Extrema (e$^-$Å^{-3})	-0.382, 1.168	-0.836, 1.398	-0.552, 0.744

Table SX2. ***Crystallographic details for complexes 9A, 9B, 9C, 9D and 9E***

	9A	**9B**	**9C**	**9D**	**9E**
CSD Submission Number	201230	2012631	2012632	2012633	2019803
Refinement Model Formula	$C_{22}H_{32}Cl_2CuN_4O_8$	$C_{22}H_{32}Cl_2CuN_4O_8$	$C_{22}H_{33.34}Cl_2CuN_4O_{8.67}$	$C_{23}H_{38}Cl_2CuN_4O_{10}$	$C_{24}H_{40}Cl_2CuN_4O_{10}$
Model Molecular Weight	614.95	614.95	626.96	665.01	679.04
Crystal System	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space Group	$P2_1/n$(#14)	$P2_1/c$(#14)	$P\bar{1}$(#2)	$P2_1/c$(#14)	$P2_1/n$(#14)
a (Å)	8.83120(10)	9.7622(2)	8.4532(2)	9.4967(7)	9.3223(9)
b (Å)	20.1287(2)	15.2121(2)	16.0765(4)	14.8226(11)	16.8722(17)
c (Å)	14.5408(2)	9.2034(2)	16.5437(4)	21.4254(15)	19.380(2)
α (º)	90	90	62.155(3)	90	90
β (º)	94.2560(10)	112.388(2)	85.199(2)	100.8900(10)	100.629(2)
γ (º)	90	90	82.390(2)	90	90
V (Å^3)	2577.65(5)	1263.72(4)	1969.82(10)	2961.7(4)	2996.0(5)
D_c (g cm^{-3})	1.585	1.616	1.586	1.491	1.505
Z	4	2	3	4	4
Crystal Size (mm)	0.18x0.16x0.08	0.27x0.165x0.10	0.12x0.04x0.02	0.219x0.182x0.073	0.396x0.306x0.242
Crystal Colour	light blue	red	violet	dark blue	dark violet
Crystal Habit	prism	prism	block	blade	prismatic
Temperature (Kelvin)	150.0(5)	150.0(5)	150.0(5)	150.0(5)	150.0(5)
λ(Mo Kα, Å)	1.5418	1.5418	1.5418	0.71073	0.71073 Å
μ(Mo Kα, mm^{-1})	3.580	3.652	3.545	0.976	0.967
$T_{min,max}$	0.605, 1.00	0.704, 1.00	0.50477, 1.00	0.6958, 0.7461	0.921, 1.00
$2\theta_{max}$ (º)	151.94	151.74	144.24º	61.02º	70.42º
hkl range	-11 11, -25 25, -17 18	-11 12, -19 19, -11 11	-10 10, -19 19, -20 20	-13 13, -21 20, -29 29	-15 15, -27 27, -31 30
N	73682	21129	70340	51703	118853
N_{ind}	5374(R_{merge} 0.0535)	2600(R_{merge} 0.0305)	7779(R_{merge} 0.0555)	8828(R_{merge} 0.0271)	12932(R_{merge} 0.0374)
N_{obs}	4781(I > 2σ(I))	2359(I > 2σ(I))	7058(I > 2σ(I))	6207(I > 2σ(I))	10651(I > 2σ(I))
N_{var}	359	169	519	368	349
Residuals* $R1(F)$, $wR2(F^2)$	0.0354, 0.0893	0.0328, 0.0844	0.0406, 0.0989	0.0715, 0.1724	0.0803, 0.2107
GoF(all)	1.161	1.358	0.972	1.035	1.172

Residual Extrema ($e^{-}Å^{-3}$)	-0.396, 0.707	-0.409, 0.822	-0.605, 0.949	-0.693, 1.209	-1.504, 1.778

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4. Figures

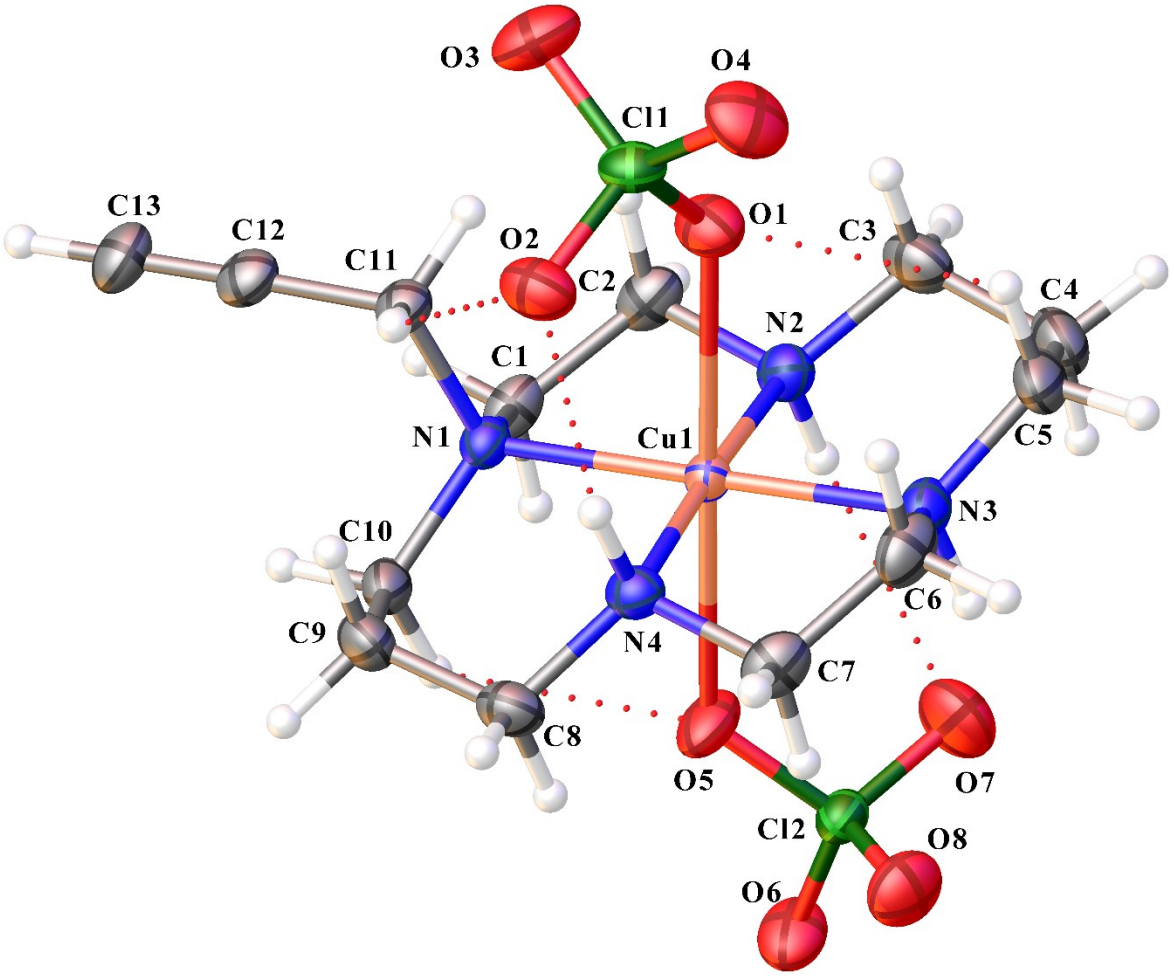

Figure SX1. Olex2[7] depiction of complex [Cu(**6**)]$(ClO_4)_2$ ***with displacement ellipsoids shown at the 50% level.***

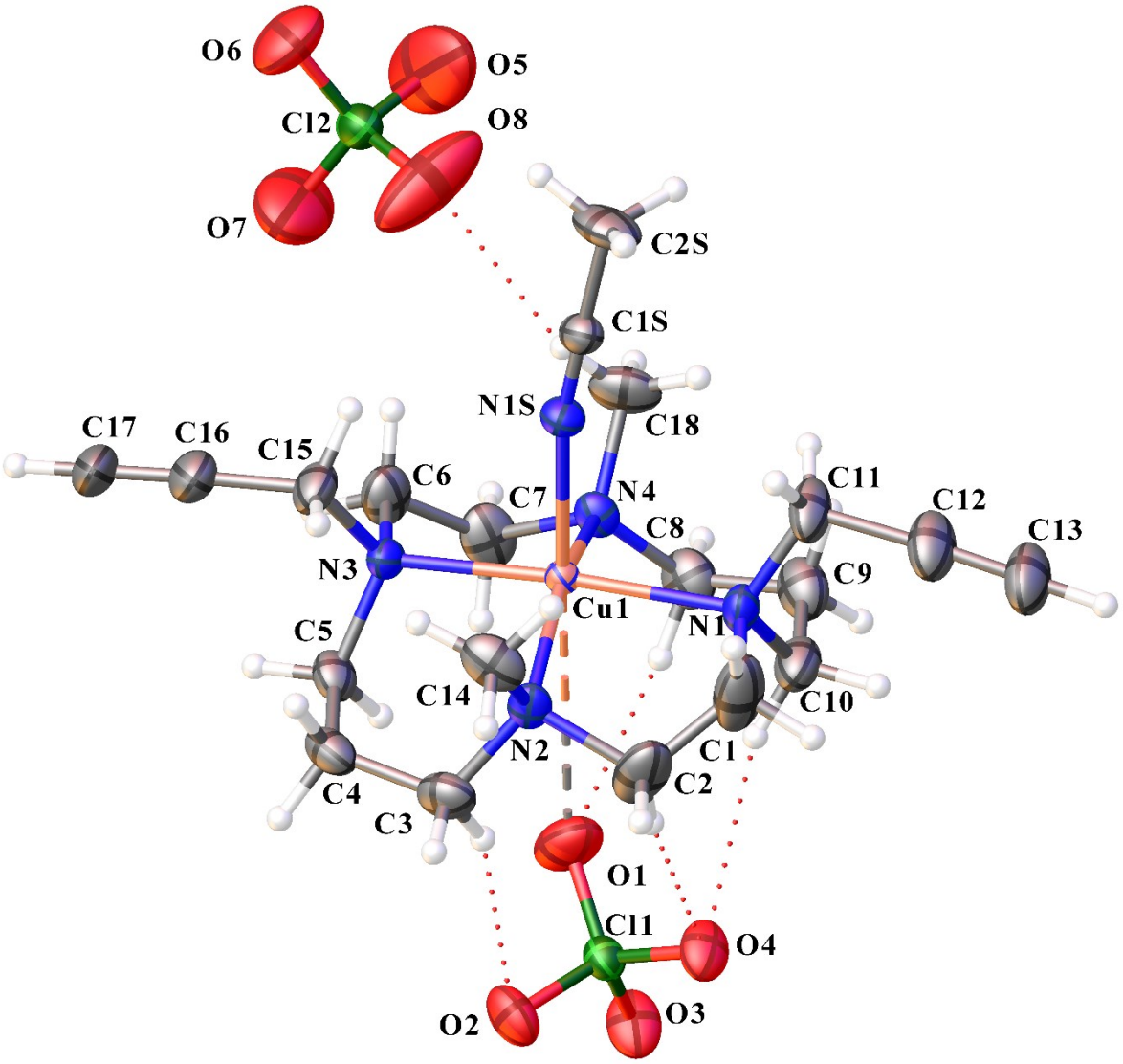

Figure SX2. Olex2[7] depiction of complex $[Cu(\mathbf{7})](ClO_4)_2$ ***with displacement ellipsoids shown at the 50% level.***

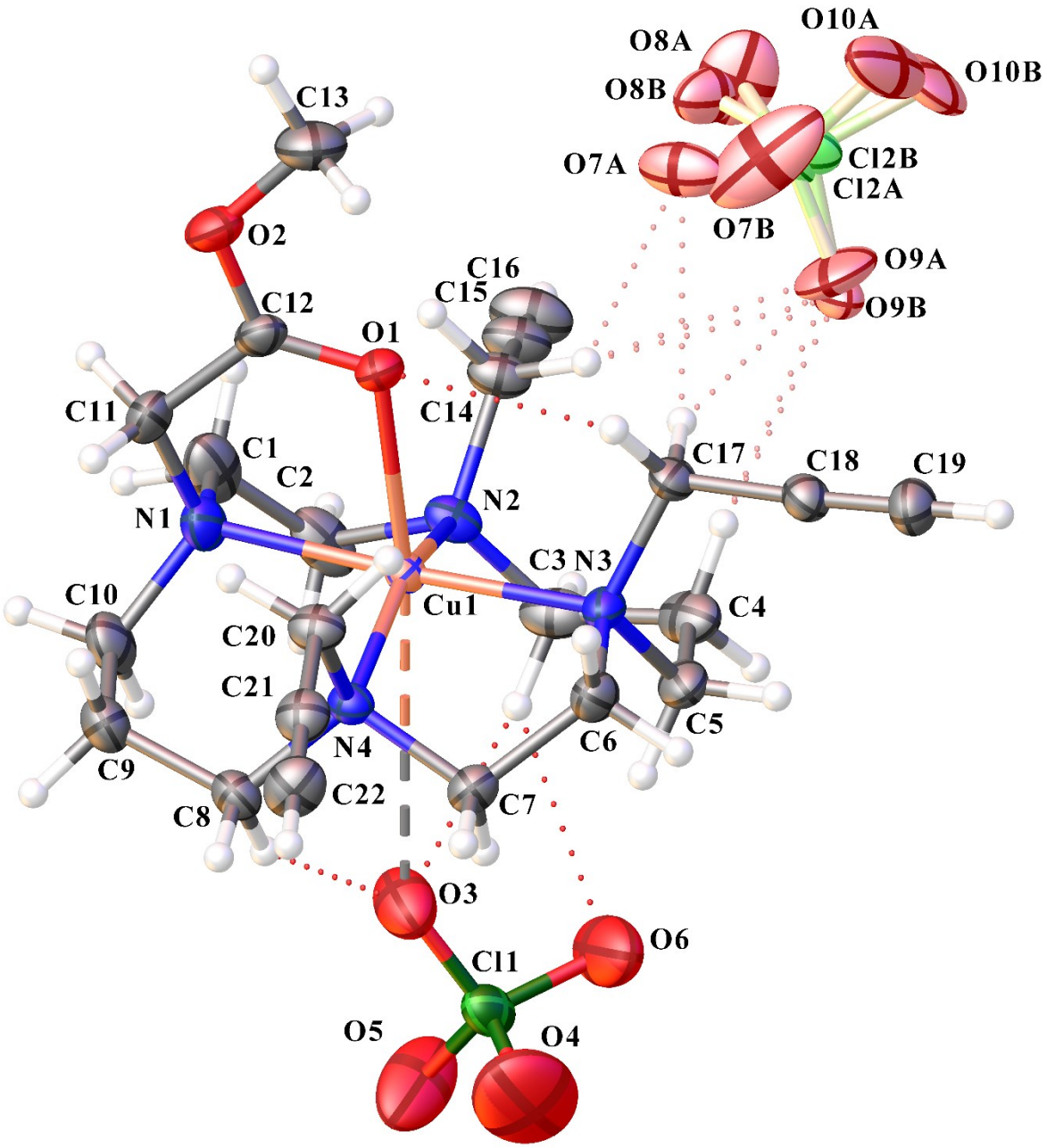

Figure SX3. Olex2[7] depiction of complex [Cu(**8**)](ClO$_4$)$_2$ ***with displacement ellipsoids shown at the 50% level and disordered sites highlighted with 'faded' colours.***

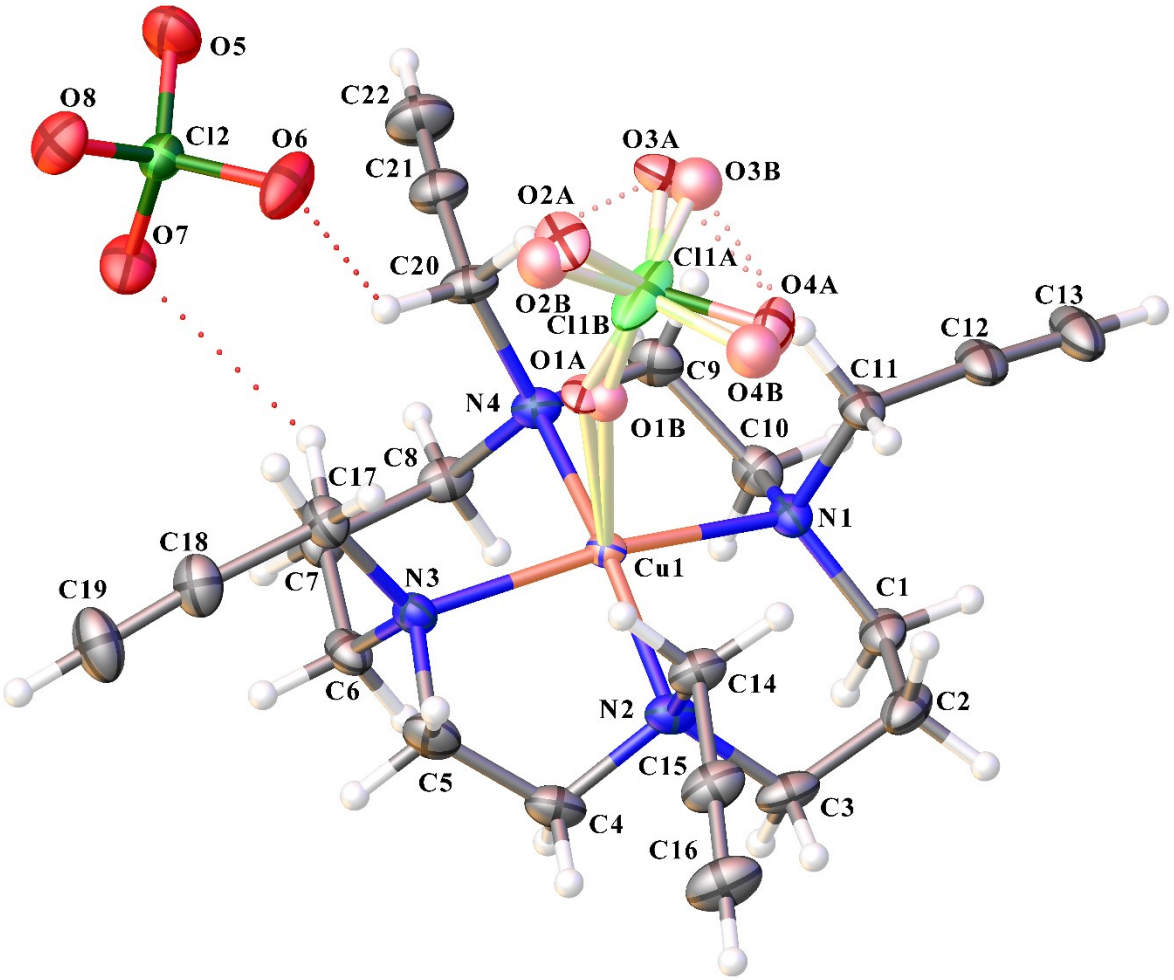

Figure SX4. Olex2[7] depiction of complex 9A with displacement ellipsoids shown at the 50% level and disordered sites highlighted with 'faded' colours.

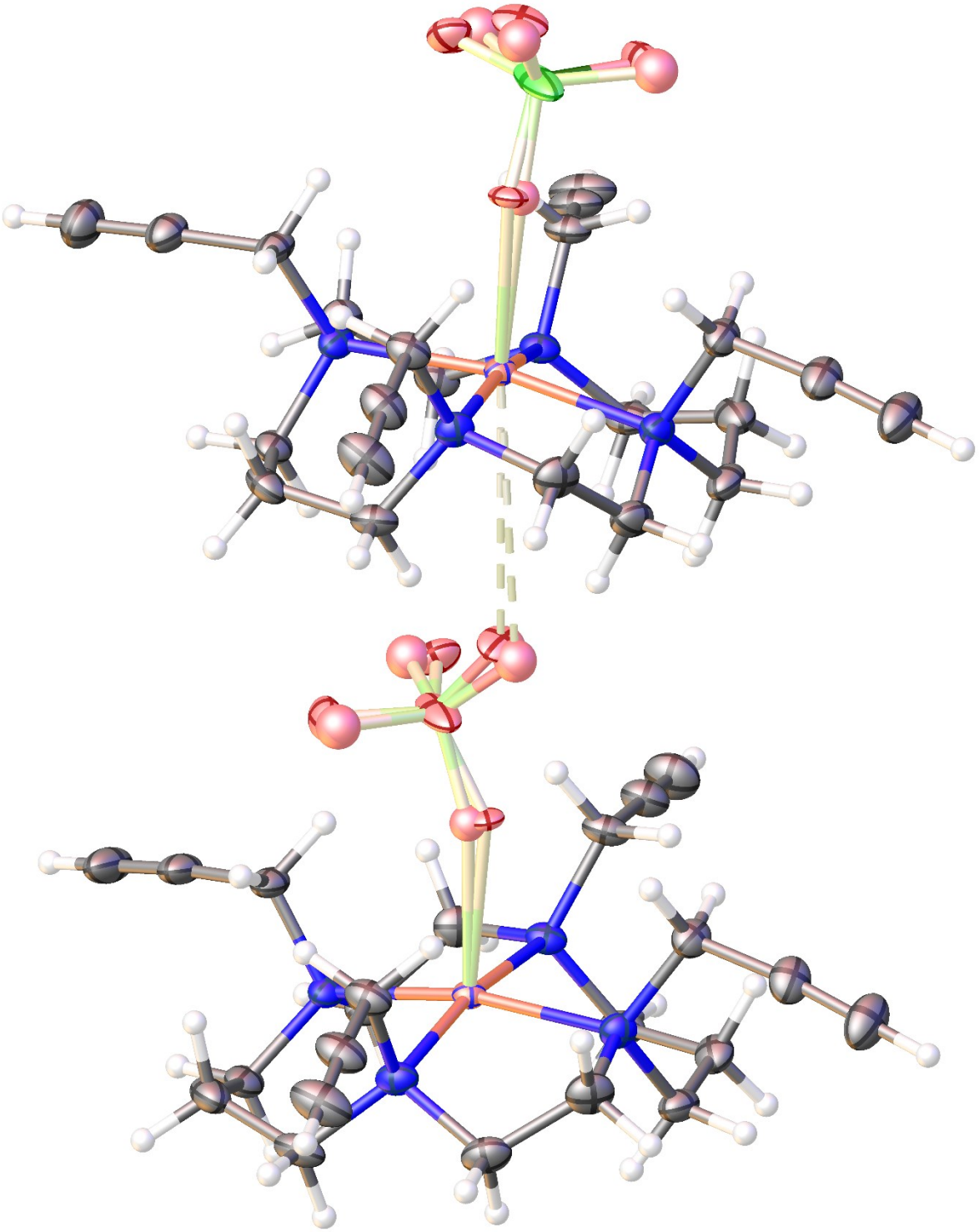

Figure SX5. Olex2[7] depiction of complex 9A with displacement ellipsoids shown at the 50% level and disordered sites highlighted with 'faded' colours.

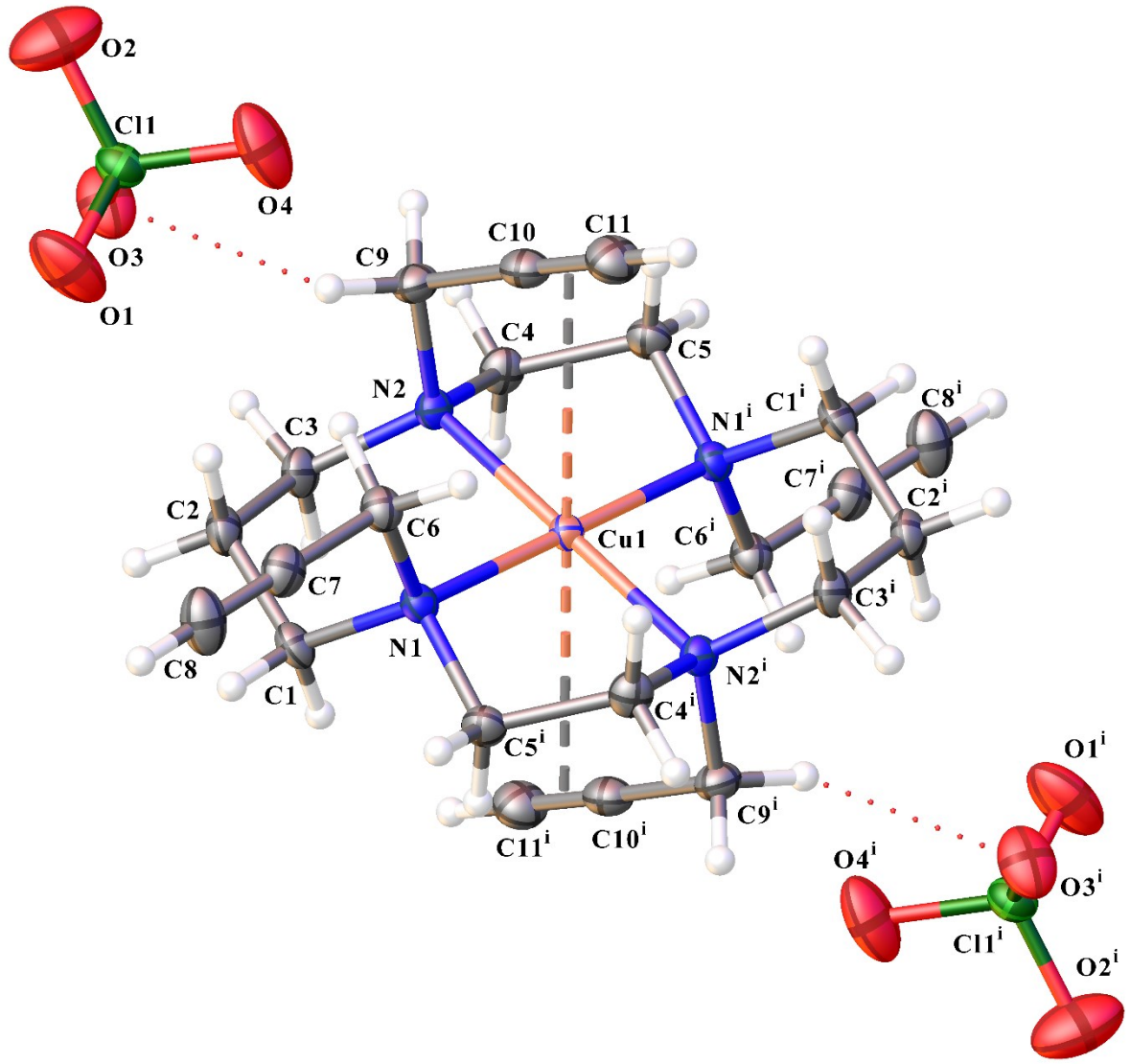

Figure SX6. Olex2[7] depiction of the structure obtained from the 9B crystal, with displacement ellipsoids shown at the 50% level. The complex dication resides on an inversion site and the superscript i denotes 1-x,1-y,1-z.

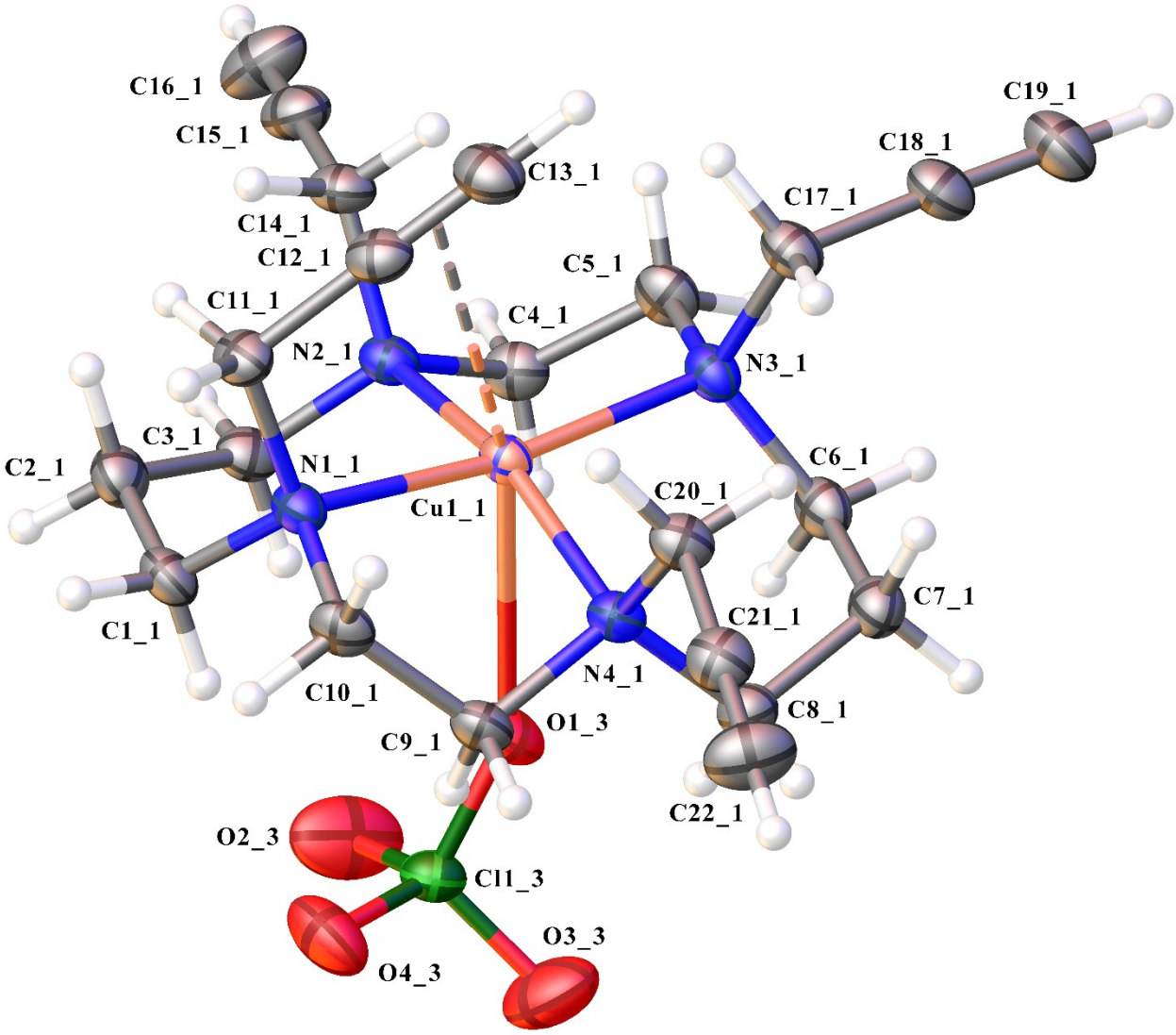

Figure SX7a. Olex2[7] depiction of complex 9C-1 with displacement ellipsoids shown at the 50%. The second perchlorate counterion is not shown.

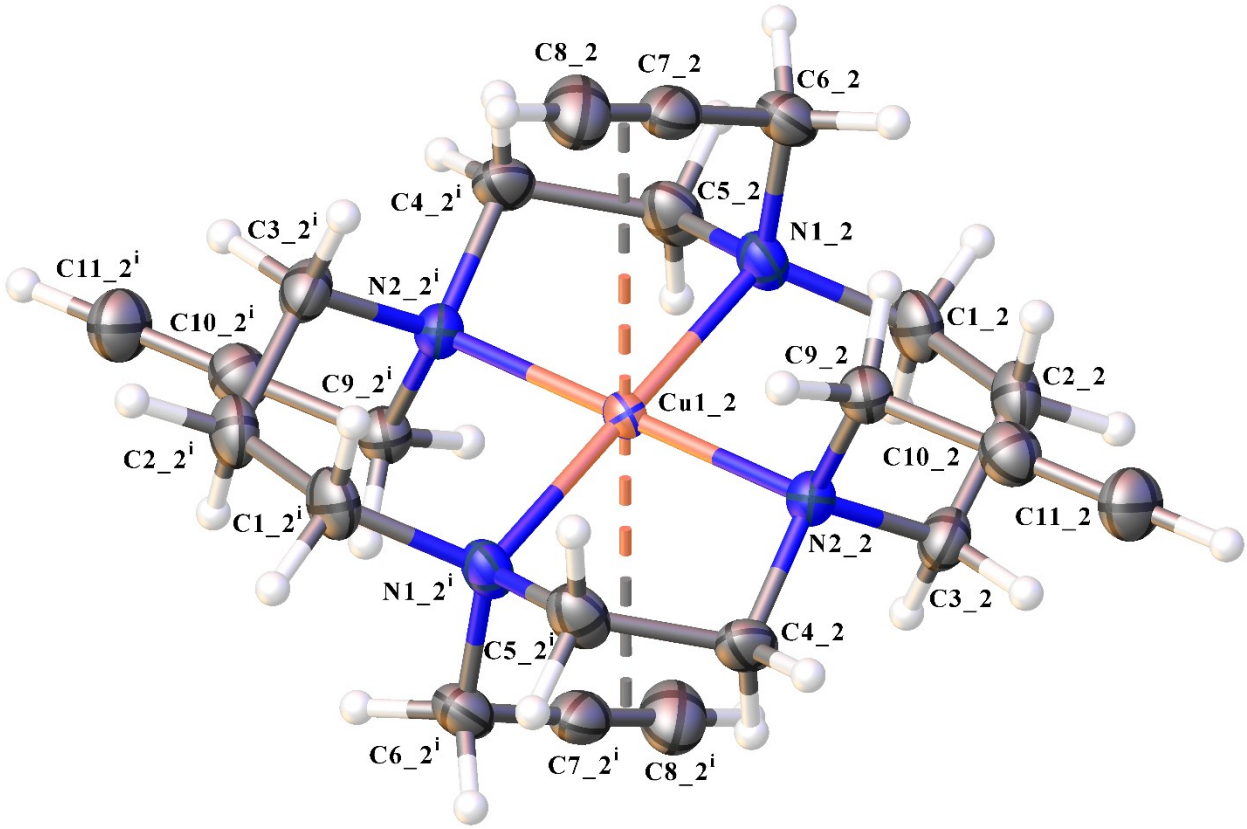

Figure SX7b. Olex2[7] depiction of complex 9C-2 with displacement ellipsoids shown at the 50%. The complex molecule is located on an inversion site and the superscript i denotes the following inversion: -x, 1-y, -z. The counterion associated with the crystallographically unique half complex molecule is not shown.

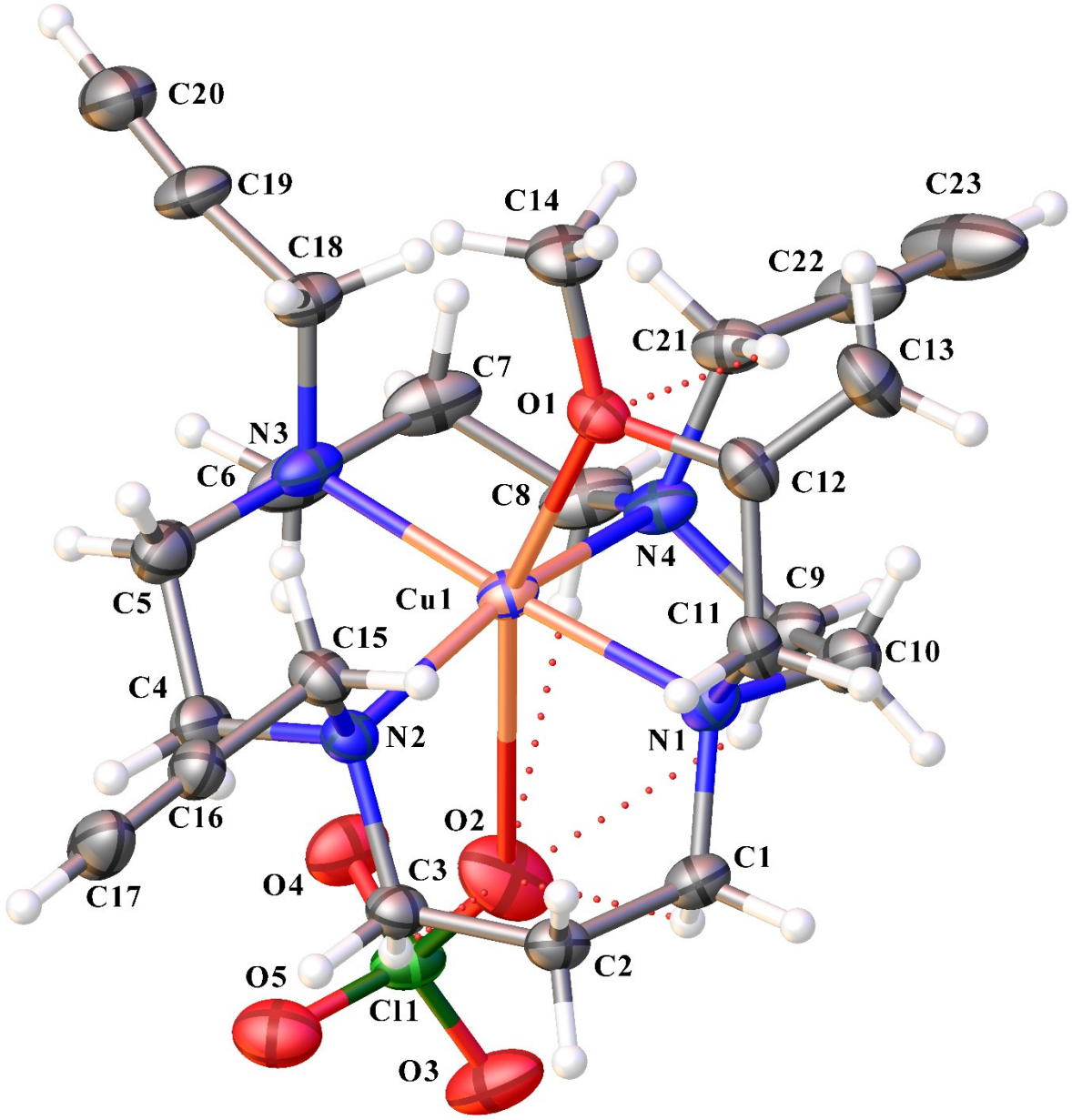

Figure SX8. Olex2[7] depiction of complex 9D with displacement ellipsoids shown at the 50%; the second counterion and a water molecule are not shown.

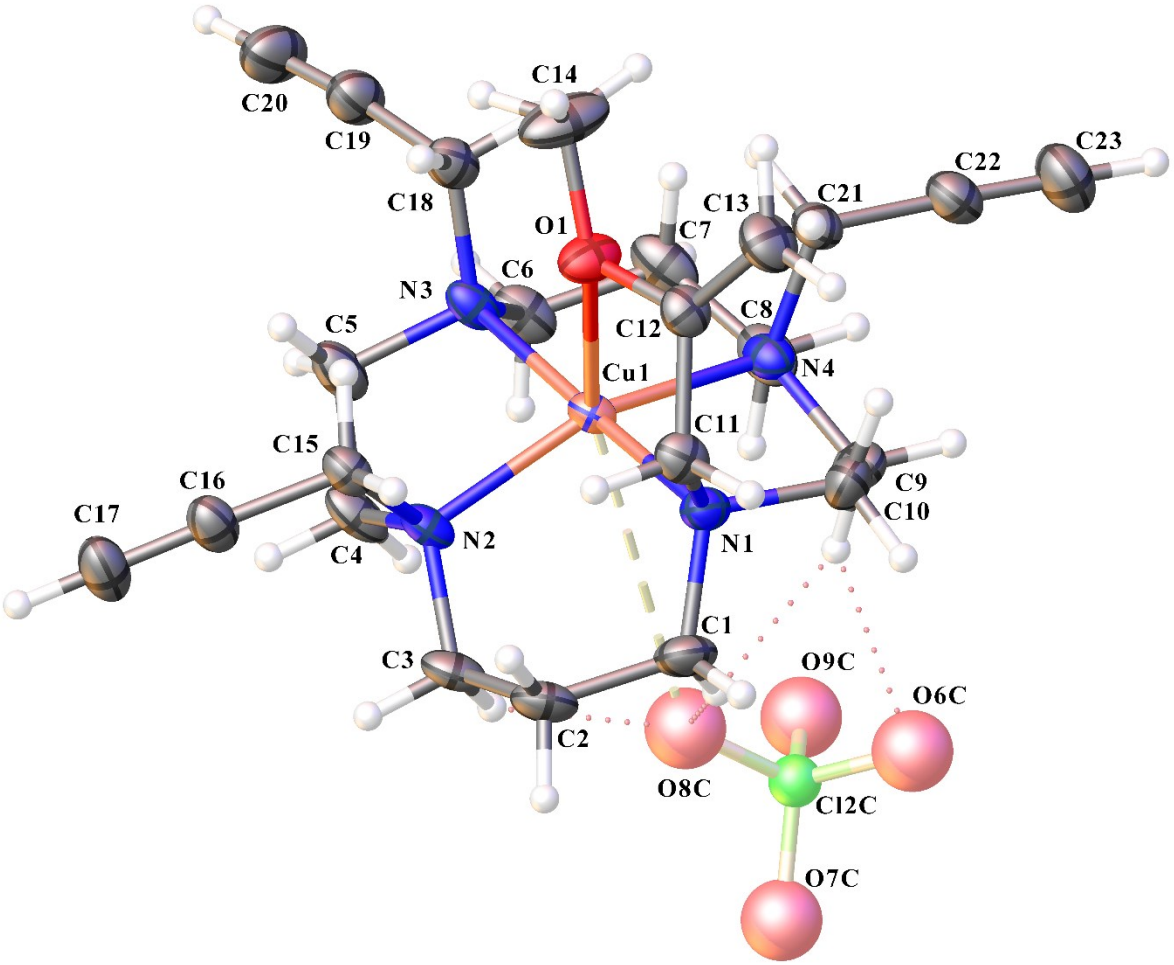

Figure SX9. Olex2[7] depiction of complex 9E with displacement ellipsoids shown at the 50% and disordered sites highlighted with 'faded' colours. One of the four orientations of a perchlorate counterion that weakly interacts with the metal ion is shown. A second disordered perchlorate and a methanol solvate molecule are note shown.