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Supporting information

Copper-Promoted Methylene C-H Oxidation to a Ketone Derivative by O₂

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Crystal structures



Figure S1. Asymmetric unit of dpeo polymorph 1 showing 50% atomic displacement ellipsoids.

There are two molecules in the asymmetric unit, linked by an intermolecular oxime-pyridine hydrogen bond. Hydrogen bonded rings comprising four dpeo molecules are linked to each other *via* π - π stacking interactions (Fig S2).



Figure S2. Unit cell of dpeo polymorph 1 viewed down the c axis. Red spheres indicate ring centroids.



Figure S3. Perspective view of dpeo polymorph 2 showing 50% atomic displacement ellipsoids.

The molecules are linked into hydrogen bonded chains running parallel to the c axis (Fig S4). There are no particularly significant inter-chain interactions.



Figure S4. Unit cell of dpeo polymorph 2 viewed down the *c* axis.

$[NiBr_2(dpeo)_2] \cdot \frac{1}{2} (EtOH) \cdot \frac{1}{2} (H_2O), (2 \cdot \frac{1}{2} (EtOH) \cdot \frac{1}{2} (H_2O))$

The structure contained severely disordered solvent modelled using SQUEEZE which detected 34 electrons in each of two 105 Å³ voids. Bearing in mind the solvents used in the synthesis and crystallisation, this was interpreted as half an ethanol molecule and half a water molecule per formula unit and these were added to the formula.

Both oxime functions are hydrogen bonded to the adjacent bromide ligands. The hydrogen atom bonded to O1 also makes a hydrogen bond to the equivalent atom under symmetry operation -x+2, -y+1, -z+1 (Fig S5, Table S1), so was modelled over two positions with 50% occupancy.



Figure S5. Inter- and intramolecular hydrogen bonding in $2 \cdot \frac{1}{2}$ (EtOH) $\frac{1}{2}$ (H₂O), 50% probability ADPs. Hydrogen bonds shown as dashed lines, hydrogen atoms not involved in H-bonding omitted for clarity.

D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A
01—H1 <i>C</i> …01 ⁱ	0.86	2.59	2.840 (4)	98
O1—H1 <i>B</i> ···Br2	0.86	2.36	3.097 (2)	144
O2—H2 <i>O</i> …Br1	0.84	2.39	3.115 (2)	145

Table S1. Hydrogen-bond geometry (Å, °) for 2.1/2(EtOH).1/2(H₂O)

Symmetry code: (i) -x+2, -y+1, -z+1.

The uncoordinated pyridine groups show $\pi-\pi$ stacking (Fig S6), the centroid-centroid distance between the ring containing N3 and that containing N6 is 3.884 Å (under $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) and there is a longer interaction with a ring containing N2 (4.020 Å under $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$).



Figure S6. π -stacking interactions involving the dangling pyridyl rings in the structure of complex **2**. The distances are measured between the centroids of the two aromatic rings involved. The hydrogens have been omitted for clarity.

[Ni(dpeo)₃](ClO₄)₂·3EtOH (3·3EtOH)

The structure contained severely disordered solvent modelled using SQUEEZE. The diffuse electron density corresponds to 149 electrons in each of two 520 Å³ voids per cell (78.5 electrons per formula unit); three ethanol solvate molecules per formula unit (78 e⁻) were included in the formula. The hydrogen atoms of the oxime group were located from difference maps and their coordinates refined. Each makes an intramolecular (but interligand) hydrogen bond to the uncoordinated pyridine of a neighbouring ligand (Fig S7, Table S2).



Figure S7. Intramolecular (but interligand) H-bonding in $[Ni(dpeo)_3](ClO_4)_2$, complex **3**. ADPs drawn at the 50% level, H-bonds shown as dotted lines.

Table S2	Hydrogen-bond	geometry	(Å,	°) for 3
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D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A
O1—H1 <i>O</i> …N9	0.83 (3)	1.95 (3)	2.728 (3)	157 (3)
O2—H2 <i>O</i> ⋯N3	0.85 (3)	1.91 (3)	2.693 (2)	154 (3)
O3—H3 <i>O</i> …N6	0.86 (3)	1.90 (3)	2.677 (3)	149 (3)

The unit cell packing (Fig S8) is dominated by a C-H $\dots\pi$ interaction between C2 and the pyridyl ring containing N3 under symmetry operation 1-x, -y, -z and by two $\pi-\pi$ stacking interactions, between the ring containing N3 and that containing N4 (under x, $\frac{1}{2}$ -y, $-\frac{1}{2}$ +z) and between the ring containing N9 and its equivalent (under 1-x, 1-y, -z).



Figure S8. π – π stacking and C-H··· π interactions in [Ni(dpeo)₃](ClO₄)₂. Red spheres indicate the centroids of the pyridyl rings involved. The perchlorate anions and hydrogen atoms (other than those involved in interactions) have been omitted for clarity.

[Co(dpeo)₃](ClO₄)₃ (4)

The structure was refined as a racemic twin in R3c (BASF 0.400(19)). The cation lies on a 3-fold axis and each dpeo ligand makes an oxime – pyridine intramolecular (but interligand) hydrogen bond (Figure S9 and Table S3). The perchlorate anion was disordered and was modelled with 55:44 occupancy of two overlapping sites.



Figure S9. Intramolecular (but interligand) H-bonding in $[Co(dpeo)_3](ClO_4)_3$, complex 4. ADPs drawn at the 50% level, H-bonds shown as dotted lines.

Table S3 Hydrogen-bond geometry (Å, °) for (4)

D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A
O1—H1 <i>O</i> …N3 ⁱ	0.79 (3)	1.90 (3)	2.646 (3)	158 (4)

Symmetry code: (i) -y+1, x-y, z.

The perchlorate anions interact weakly with a number of C-H bonds but, other than these, there are no very striking intermolecular interactions in the lattice.



Figure S10. View down the c axis, complex 4.

[Fe^{III}Fe^{II}₂(dpeo-H)₃(dpeo)₃](PF₆)₄·2EtOH·3H₂O (5)

The iron(III) ion Fe2 sits on a centre of symmetry and links two *fac*-coordinated Fe(II) L3 units. One of the two independent PF_6^- ions showed disorder which was modelled as rotation about the F7-P2-F8 axis. There was some poorly defined electron density in the cell which was treated using SQUEEZE (which estimated 40 electrons in a single 194Å void in the cell); this electron density was not added to the cell contents.



Figure S11. Asymmetric unit of complex 5. ADPs drawn at the 50% level. H atoms omitted for clarity, H-bonds shown as dotted lines.

The iron ions (1Fe^{III} and 2Fe^{II}) have a total positive charge of +7 per formula unit and there are 4 PF_6^- ions per formula unit; the remaining 3 positive charges come from protonation of the "dangling" pyridines. Of these, N3 makes a hydrogen bond to the ethanol solvate molecule, which is also H-bonded to an oxime O3ⁱⁱ atom (Table S4); this NH proton was located in difference maps. Pyridine nitrogen N6 is not within H-bonding distance of any H-bond acceptor and is therefore unlikely to be protonated. Consequently, charge balance requires that the remaining pyridine nitrogen, N9, be disordered (i.e. 50% protonated). N9 is Hydrogen bonded to a water molecule (O5) and the disorder can be accommodated by combining it with a disorder of one of the water hydrogen atoms over two sites (Figure S12). In effect the disorder only affects the positions/occupancies of two hydrogen atoms.

The packing diagram (Fig S13) shows an edge-to-edge π -interaction between the pyridine rings containing N3 of adjacent molecules (3.387 Å)



Figure S12. Disorder components for H atom bonding.

Table S4. Hydrogen-bond geometry (Å, °) for (5)

D—H···A	D—H	H···A	$D \cdots A$	D—H···A
N3—H3 <i>N</i> ···O4	0.88	1.84	2.647 (3)	152
N9′—H9′…O5′	0.88	1.82	2.669 (5)	161
O5—H5 <i>C</i> ⋯N9	0.85 (2)	1.83 (4)	2.669 (5)	168 (14)
O5—H5 <i>D</i> ⋯O6	0.87 (1)	2.01 (5)	2.633 (8)	128 (5)
O5'—H5C'…F12'	0.85 (2)	2.42 (3)	3.210 (9)	154 (5)
O6—H6 <i>D</i> ···F2 ⁱ	0.81 (2)	2.45 (8)	2.975 (7)	123 (8)
O6—H6 <i>C</i> ⋯F4	0.80 (2)	2.46 (8)	3.042 (5)	131 (9)
O6—H6 <i>C</i> ⋯F8	0.80 (2)	2.29 (6)	2.957 (6)	142 (9)
O4—H4 <i>A</i> …O3 ⁱⁱ	0.81 (4)	1.91 (4)	2.718 (3)	173 (4)

Symmetry codes: (i) -x, -y, -z; (ii) -x+2, -y+1, -z+1.



Figure S13. Packing diagram for complex **5** viewed down the *a* axis. Red dots indicate the centres of bonds involved in edge-to-edge overlap.

[Cu(dpeo)₂](ClO₄)₂ (6)

The hydrogen atom on pyridine nitrogen N6 was located from difference maps and the coordinates refined. The two oxime oxygen atoms O1 and O2 are within H-bonding distance (2.449 (4) Å, Table S5), the (single) H atom was not located and has been placed with 50% occupancy at two calculated positions, one on each oxygen (Fig S14). The pendant protonated pyridine hydrogen bonds to a second cation (N6 – N3 3.038 (6) Å under -x+1, -y, -z+1), forming a dimer (Fig S15, Table S5).



Figure S14. Structure of $[Cu(dpeo)_2](ClO_4)_2$ (5). Atoms shown as 50% probability ADPs, H atoms bonded to O1 and O2 have 50% site-occupancy



Figure S15. H-bonded dimeric structure of the cations from $[Cu(dpeo)_2](ClO_4)_2$ (5). For clarity, only one of the disordered oxime hydrogen atoms is shown and H-atoms not involved in are omitted.

One of the perchlorate anions makes no significant interactions with the cation, the other is coordinated to the copper ion (Cu – O5 2.458(3) Å and has a weaker interaction with a second copper (Cu1 – O3 2.810(4) Å under x-1, y, z), generating a chain (Fig S16). The combination of this interaction with the hydrogen bonding and π – π interaction between the pyridyl rings containing N3 and N6 (centroid-centroid 3.925 Å under 2-x, -y, 1-z) results in columns running parallel to the *a* axis (Fig S17). Neighbouring columns are linked by π – π stack between pairs of pyridyl rings containing N4 (centroid-centroid 3.998 Å under 1-x, 1-y, -z) and pairs of rings containing N4 (centroid-centroid 3.968 Å under 1-x, -y, -z) (Fig S17).



Figure S16. Section of the perchlorate-bridged polymer chain. Atoms shown as 50% probability ADPs, H atoms omitted for clarity.

Table S5. Hydrogen-bond geometry (Å, °) for 6.

D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A
O1—H1 <i>O</i> ⋯O2	0.84	1.63	2.449 (4)	163
O2—H2 <i>O</i> ⋯O1	0.84	1.64	2.449 (4)	162
N6—H6⋯N3 ⁱ	0.85 (5)	2.19 (5)	3.038 (6)	172 (5)

Symmetry code: (i) -x+1, -y, -z+1.



Figure S17. Combination of H-bonding, perchlorate bridging and π - π stacking forming columns.



Figure S18. Packing diagram viewed down the *a* axis.

[Cu(bpca)(hidpe)](ClO₄)·1¹/₃EtOH (7·1.33EtOH)

 $[Cu(bpca)(hidpe)](ClO_4)$ crystallised in R^3 with large channels running parallel to the *c* axis (Figure S19). These contained diffuse electron density and SQUEEZE detected to 3 voids of 918, 922 and 924 Å³, each containing 208 electrons. This was assigned to 8 ethanol molecules per void, or 1.333 per formula unit.



Figure S19. Unit cell packing for 6 viewed down the *c* axis and showing the channels where diffuse electron density was located.

The oxime hydrogen atom was located in difference maps but, since this was a weak data set, it were subsequently inserted at a calculated position, riding on the carrier oxygen atom. The oxime OH group makes hydrogen bonds with the two oxygen atoms of a neighbouring hidpe ligand (under symmetry operation -x+4/3, -y+5/3, -z+5/3, Table S6), linking the molecules into dimeric units (Figure S20). The carbonyl of the bpca molecule is not involved in H-bonding to other cations or anions but is located in the sides of the channels (Figure S21) and is likely to interact with the disordered solvent.

Table S6. Hydrogen-bond geometry (Å, °) for 7.

D—H···A	<i>D</i> —Н	H···A	$D \cdots A$	D—H···A
O1—H1 <i>O</i> ⋯O3 ⁱ	0.84	2.47	3.147 (3)	138
O1—H1 <i>O</i> ⋯O4 ⁱ	0.84	1.93	2.645 (3)	142

Symmetry code: (i) -x+4/3, -y+5/3, -z+5/3.



Figure S20. Hydrogen bonding and weakly coordinating perchlorate anion in the crystal structure of [Cu(bpca)(hidpe)](ClO₄).



Figure S21. C-H \cdots π interaction linking cations around a channel. Perchlorate groups and hydrogen atoms not involved in the interaction are omitted for clarity.

The most striking intramolecular feature is a C-H··· π interaction linking hidpe ligands in a hexagonal pattern which defineds the large cavities running parallel to the *c* axis (Figure S21). The H····centroid distance between C23-H23 and the centroid of the ring containing N4 is 2.684 Å, under symmetry operation -1/3+y, 1/3-x+y, 1/3-z.

ESI mass spectrometry



Figure S22. ESI mass spectrum of the compound [Cu(dpeo)₂](ClO₄)₂ (6) redissolved in acetonitrile.



Figure S23. Fitting of the observed peak (black) with the species $[Cu^{I}(dpeo)]^{+}$. The copper(II) has been fully reduced to copper(I) here.



Figure S24. Fitting of the observed peak (black) with a mixture of species with two different oxidation states for the Cu centre: $[Cu^{I}(dpeo)_{2}]^{+}$ (red) and $[Cu^{II}(dpeo)(dpeo-H)]^{+}$ (green) relative ratio are approximately 2:1.



Figure S25. ESI mass spectrum of a solution containing dpeo + a large excess of H_2O_2 in an ethanol/ H_2O 50/50 solution. The spectrum was measured after 2 days.

FTIR Spectroscopy



Figure S26. IR spectrum of some crystals of the complex [Ni(dpeo)₃](ClO₄)₂.



Figure S27. FTIR spectrum of the crystals of the complex [NiBr₂(dpeo)₂].



Figure S28. FTIR spectrum of the compound [NiCl₂(dpeo)₂].



Figure S29. FTIR spectrum of the compound [Co(dpeo)₃](ClO₄)₃. IR (cm⁻¹) v_{max}: 1625 (w), 1602 (m), 1566 (w), 1538 (w), 1507 (w), 1464 (s), 1437 (m), 1414 (m), 1335 (w), 1308 (w), 1266 (w), 1224 (m), 1199 (m), 1167 (w), 1079 (s), 1024 (m), 996 (m), 962 (w), 945 (w), 875 (w), 819 (w), 764 (m), 748 (w), 689 (w).



Figure S30. FTIR spectrum of the compound [Fe₃(dpeo-H)₂(dpeo)₄](PF₆)₅·EtOH·2H₂O.



Figure S31. FTIR spectrum of the compound [Cu(dpeo)₂](ClO₄)₂.



Figure S32. FTIR spectrum of the compound [Cu(bpca)(hidpe)](ClO₄).



Figure S33. FTIR spectrum of the compound [Cu(pic)₂(H₂O)].

Additional scheme



Scheme S1. Formation of Hbpca via hydrolysis of tpt.