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PAPER

When is an imine not an imine? Unusual reactivity of a series of Cu(II) imine-pyridine complexes and their exploitation for the Henry reaction†

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In this paper we report the synthesis and solid-state structures for a series of pyridine based Cu(II) complexes and preliminary data for the asymmetric Henry reaction. Interestingly, the solid-state structures indicate the incorporation of an alcohol into one of the imine groups of the ligand, forming a rare α-amino ether group. The complexes have been studied *via* single crystal X-ray diffraction, EPR spectroscopy and mass spectrometry. Intriguingly, it has been observed that the alcohol only adds to one of the imine moieties. Density functional theory (DFT) calculations have also been employed to rationalise the observed structures. The Cu(II) complexes have been tested in the asymmetric Henry reaction (benzaldehyde + nitromethane or nitroethane) with ee's up to 84% being achieved as well as high conversions and modest diastereoselectivities.

Introduction

The use of imines (C═N) as ligands in coordination chemistry and catalysis is ubiquitous.[1] This is simply because imines are versatile ligands and can bind to many metal centres. In the preparation of such metal complexes alcohol solvents (in particular MeOH and EtOH) are commonplace and it is generally assumed that the solvent is innocent in terms of reactivity. However, under certain circumstances these labile azomethine linkages can be susceptible to attack by alcohols to generate *O*-alkyl hemiaminals. Such species are believed to be short lived intermediates in the formation of imines.[2] Very recently, and for the first time, Fujita was able to crystallographically characterise a transient hemiaminal trapped in a porous Zn(II) network.[2] However, pertinent to this study are the very limited crystallographically characterised examples of such ligated species. Notable examples include those of Pregosin (Pt),[3] Hoskins (Cu),[4] Rybak–Akimova (Cu)[5] and Mitra (Ni)[6] where the coordination of the metal ion is believed to stabilise the highly reactive α-amino ether.

Cu(II) complexes have been extensively utilised in the asymmetric Henry (nitro aldol) reaction.[7] For example, Bandini *et al.* have utilised a series of C_2-symmetrical oligothiophene ligands for this reaction.[8] Blay and co-workers have applied C_1-symmetric camphor derived amino pyridine ligands with high ee's being observed.[9] Sparteine Cu(II) complexes have been shown to be selective for this reaction.[10] Oxazolines, imines and amine ligands with Cu(II) have also been exploited for this reaction.[11] However, Cu(II) is by no means the only metal centre that will catalyse this process Zn(II),[12] Cr(III),[13] La(III)[14] and Co(II)[15] are active for this transformation.

In this paper we have prepared a series of Cu(II) complexes based on Schiff base pyridine ligands where the solvent has played a key role in the formation of unexpected products. In some instances the alcohol solvent has reacted with one of the imine groups of the ligand to form an α-amino ether group. The nature of the alcohol has been varied to study this effect in more detail.

Results and discussion

Ligand and complex preparation

As part of our on going investigations into the use of Cu(II) complexes in asymmetric catalysis we were interested in the coordination chemistry of ligands **L1–L4**, Scheme 1 and 2.[11d] These ligands were readily prepared by the reaction of (1*R*,2*R*)-diaminocyclohexane with pyridine-2-carboxaldehyde or 6-methyl-2-pyridine carboxaldehyde and reduction with $NaBH_4$ where appropriate. All ligands were characterised by multi-nuclear NMR spectroscopy and HR-MS.

Ligand **L1** was reacted with one equivalent of $Cu(OTf)_2$ in methanol, in anticipation of generating Cu(**1**)$(OTf)_2$, Scheme 2. However, this was not the case and instead methanol added across one imine and [Cu(**1**-MeOH)]$(CF_3SO_3)_2$ was isolated, Scheme 2. The cation is shown in Fig. 1, in-which one of the imine groups of the ligand has reacted with MeOH to form the rare α-amino ether moiety. Selected bond lengths for all complexes prepared are shown in Table 1.

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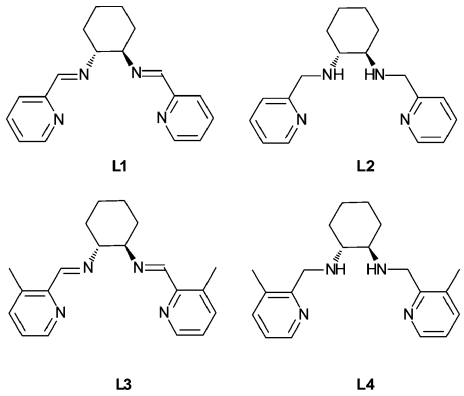
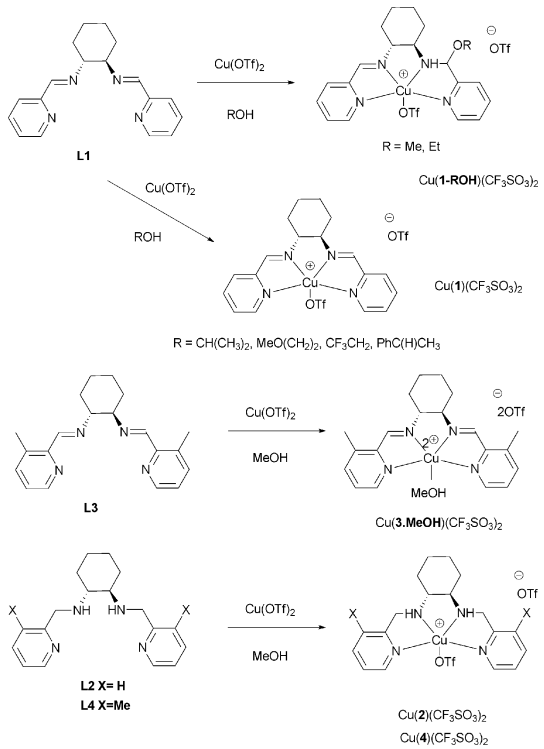


Scheme 1 Ligands used in this study.



Scheme 2 Novel Cu(II) complexes prepared in this study.

In the solid-state there are two crystallographically unique Cu(II) centres both with a square planar arrangement of nitrogen atoms and a weakly coordinating triflate anion completing the coordination sphere of the metal. For one of the Cu(II) centres the addition of MeOH across the imine was 100% as indicated by the fact that this was fully occupied in the crystal structure. Whereas for the other Cu(II) centre the occupancy of the alcohol group was 40%. This is exemplified by the N(3)–C(13) distance of 1.450(7) Å, indicative of a nitrogen-carbon single bond, in the fully occupied system. Whilst, in the partially occupied system this distance is 1.358(8) Å; thereby averaging a C–N and C=N bond length. Also of note was that only one Schiff base group of each ligand reacted with the alcohol solvent.

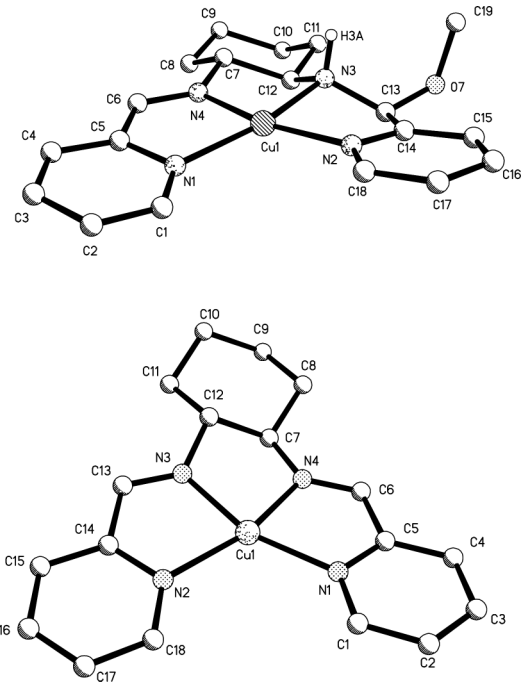


Fig. 1 Top: Molecular structure of the cation $[Cu(\mathbf{1}\text{-MeOH})]^{2+}$ Bottom: Molecular structure of the cation $[Cu(\mathbf{1})]^{2+}$ prepared from IPA. In both cases the triflate anions all H atoms (except H3A) have been removed for clarity.

Upon reaction with MeOH a new chiral centre was generated at C(13), which has the *S* configuration. In the MS a peak at 504.0473 was observed corresponding to $[Cu(\mathbf{1})\cdot CF_3SO_3]^+$ and a major peak at 536.0745 assigned as $[Cu(\mathbf{1}\text{-MeOH})\cdot CF_3SO_3]^+$ was also detected, Scheme 2. In the MS there was no peak due to the addition of MeOH to both imine moieties. As expected for an MS run in CD_3OD a mass at 539.0925 was detected, presumably the initially formed N–D is labile and exchanges with free H^+ in the mass spectrometer. Spurred on by this result the reaction

Table 1 Selected bond lengths for complexes prepared in this work

Ligand					L1 (Solvent)[a]			L2	L3
Cation (solvent)[a]	$[Cu(\mathbf{1}\text{-MeOH})]^{2+}$	$[Cu(\mathbf{1}\text{-EtOH})]^{2+}$	$[Cu(\mathbf{1}\text{-IPA})]^{2+}$	$[Cu(\mathbf{1}\text{-MeO-}(CH_2)_2OH)]^{2+}$	$[Cu(\mathbf{1}\text{-CF}_3\text{-CH}_2OH)]^{2+}$	$[Cu(\mathbf{1}\text{-C}_6H_5\text{-CH(OH)CH}_3)]^{2+}$	$[Cu(\mathbf{1})\text{-MeOH+AcOH})]^{2+}$	$[Cu(\mathbf{2})]^{2+}$	$[Cu(\mathbf{3}\cdot\text{MeOH})]^{2+}$
Cu(1)–N(1)	2.054(5)	2.056(5)	2.018(5)	2.000(8)	2.044(10)	2.032(2)	2.045(4)	2.006(4)	2.035(4)
Cu(1)–N(2)	1.993(5)	1.994(6)	2.036(6)	2.043(9)	2.047(11)	1.958(2)	1.982(4)	1.995(3)	2.038(4)
Cu(1)–N(3)	2.035(5)	2.024(5)	1.950(5)	1.939(8)	1.964(11)	—	2.020(4)	2.002(3)	1.940(3)
Cu(1)–N(4)	1.955(5)	1.948(6)	1.965(5)	1.968(8)	1.942(10)	—	1.943(4)	1.993(3)	1.956(4)
N(3)–C(13)	1.450(7)	1.475(7)	1.266(8)	1.259(12)	1.275(16)	—	1.448(5)	1.453(5)	1.277(5)
N(4)–C(6)	1.284(8)	1.251(9)	1.268(8)	1.275(11)	1.276(14)	1.258(3)[b]	1.273(6)	—	1.264(5)

[a] For complexes prepared from **L1** the solvent is that used to prepare and crystallise the sample, see Scheme 2. [b] Due to symmetry this in N(2)–C(6).

was repeated in EtOH and again it was observed that the solvent had added to only one of the imine moieties. The structure is analogous to that formed in MeOH, with two crystallographically unique Cu(II) centres-one with a fully occupied alcohol group and another with a partially occupied alcohol moiety. Again the Cu(II) centres have a square planar arrangement of nitrogen atoms and a weakly coordinating anion. In the MS the α-amino ether species was observed at 550.0919. As with the previous case a new chiral centre was observed at C(13) which is again the *S* form. If isopropanol (IPA) was employed then no α-amino ether product was observed in the solid state and Cu(**1**)$(CF_3SO_3)_2$ was isolated (Fig. 1 and Scheme 2). However, a small peak for the ether was observed in the MS. Interestingly, if a racemic form of 1-phenyl ethanol was utilised as the solvent then no α-amino ether was detected. However, is it noteworthy that the crystal was chirally enriched, with the solvent of crystallisation being 75% *S* enantiomer and 25% *R* enantiomer. This lack of formation of the α-amino ether species is presumably due to the extra steric bulk of these alcohols hindering its formation. The reaction was repeated with the electron withdrawing alcohols $MeO(CH_2)_2OH$ and CF_3CH_2OH, which are more acidic *but* less nucleophilic, in an attempt to shed additional light on the reactivity. It was hypothesised that there are two possible mechanisms of attack i) the alcohol dissociates in solution and the anion (RO^-) then attacks the carbon of the imine or ii) the alcohol first pre-coordinates to the metal centre and then attacks the imine. When more acidic alcohol solvents were employed no α-amino ether product was observed which indicates that pre-coordination of the alcohol is potentially involved. In an attempt to form the structure in which both alcohols are fully occupied in the solid state the complexation was also performed in a MeOH/acetic acid mixture (9 : 1). As before there were two crystallogaphically unique Cu(II) centres. The occupancy of the added alcohol was now 100% for both Cu(II) cations. In this case the N(3)–C(13) bond length was 1.448(5) and in the other Cu(II) cation the analogous length was 1.431(6) Å. The Cu(II) complexes formed with **L1** were analysed *via* EPR spectroscopy in MeOH, EtOH and IPA which all showed similar g and A values to eachother and analogous Cu(II) complexes in the literature.[16] Elemental analysis was consistent with the addition of MeOH being the bulk crystallised product and the MS of the solution after crystallisation and the crystals were identical. A pXRD of the crude product (before recrystallisation) is analogous to that determined from the crystal data, implying that methanol addition is occurring on a significant scale, with this ligand system.

The α-amino ether species were probed *via* DFT calculations, see Table 2 and Supporting Information for details on the LUMOs and HOMOs for the respective Cu(II) species. The calculations clearly showed that the addition of MeOH was energetically favourable. The addition of EtOH was seen to be energetically neutral, but given it is present in large excess this addition can be observed. From the calculations it is seen that addition of ^{i}PrOH to the imine is unfavourable, supporting our empirical observations. In all cases the new chiral centre at C(13) is *S*. From DFT calculations the formation of the *R* diastereoisomer is much higher in energy (+22.9 kJ mol^{-1}) and this is presumably why only one form is detected in the solid-state. However, the addition of a methoxy group to both imine groups is predicted to be thermodynamically feasible. However, even under reflux conditions we were unable to assist the production of this species with no trace being observed in the mass spectrum. Therefore, it is assumed that this species is kinetically not favourable.

Table 2 Energies calculated from DFT[a]

Cation	ΔE/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}
[Cu(**1**)]$^{2+}$	0	0	0
[Cu(**1**-MeOH)]$^{2+}$	−88.6	−73.1	−11.3
[Cu(**1**-MeOH)]$^{2+,b}$	−62.7	−50.0	+11.6
[Cu(**1**-$MeOH_2$)]$^{2+,c}$	−152.5	−126.1	−15.9
[Cu(**1**-EtOH)]$^{2+}$	−69.8	−56.2	+0.6
[Cu(**1**-^{i}PrOH)]$^{2+}$	−62.2	−46.7	+9.8

[a] See supporting information for full details of the analysis. [b] Energy for the other diastereoisomer-*R* at C(13). [c] Energy for the double addition of MeOH.

Unsurprisingly, with the reduced ligand **L2** Cu(**2**)$(CF_3SO_3)_2$ was formed, Scheme 2. In this case the Cu(II) centre has a square planar arrangement of nitrogen atoms and a weakly coordinating anion. In an attempt to gain more of an understanding into the methanol addition process the Cu(II) complex of ligand **L3** was prepared in MeOH, Fig. 2:

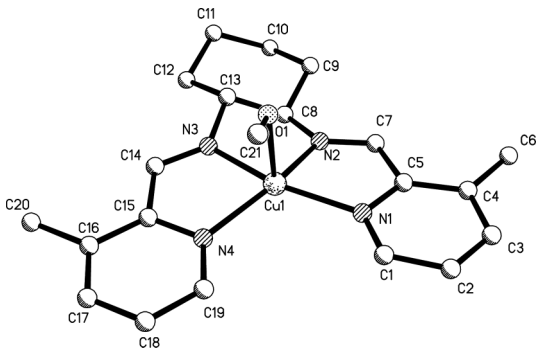


Fig. 2 Molecular structure of the cation [Cu(**3**·MeOH)]$^{2+}$ the triflate anions have been removed for clarity. This was recrystallised in MeOH.

In this case the solid-state product included a coordinated MeOH moiety and the imine was left intact. Analysis of the product *via* MS indicated there was only a trace amount of the α-amino ether species present. This is presumably related to the extra degree of steric bulk caused by the addition of the *ortho* methyl group on the pyridine ring.

Catalysis

The complexes described, together with Cu(II) complexes formed with ligands shown in Scheme 3 were tested for the asymmetric Henry reaction with benzaldehyde and either nitromethane or nitroethane. The results of which are shown in Tables 3 and 4. As a direct comparison we have prepared Cu(II) complexes of related ligands, Scheme 3.[7h,8] Complexes based on **L9** have been shown by Bandini to be very effective catalysts for this reaction. Interestingly, they observed that the unsaturated version of the ligand afforded no enantioselectivity.[8] Ligands **L6** and **L8** have been shown to form supramolecular arrays with Cu(II) in the solid state with bridging pyridine moieties.[7h] However, the related furan ligand, **L10**, has not been previously exploited for this reaction.

Table 3 Catalytic results for the Henry reaction with nitromethane[a]

Catalyst prepared from[b]	Solvent	*T*/°C	Con/%[c]	ee[d]
L1	MeOH	20	50	42
L1	MeOH	0	34	34
L1	EtOH	20	40	33
L1	IPA	20	27	19
L2	MeOH	20	98	4
L3	MeOH	20	18	2
L4	MeOH	20	44	5
L5	MeOH	20	82	26
L6	MeOH	20	95	26
L7	MeOH	20	74	1
L8	MeOH	20	96	46
L9	MeOH	20	94	37
L9	MeOH	0	94	80
L10	MeOH	20	96	57
L10	MeOH	0	95	84

[a] Catalyst:benzaldehyde:Nitromethane molar ratio employed was 0.05 : 1 : 10, [b] see Scheme 2 and 3; [c] conversion as determined by ^{1}H NMR spectroscopic analysis, [d] determined by chiral HPLC.

Table 4 Catalytic results for the Henry reaction with nitroethane[a]

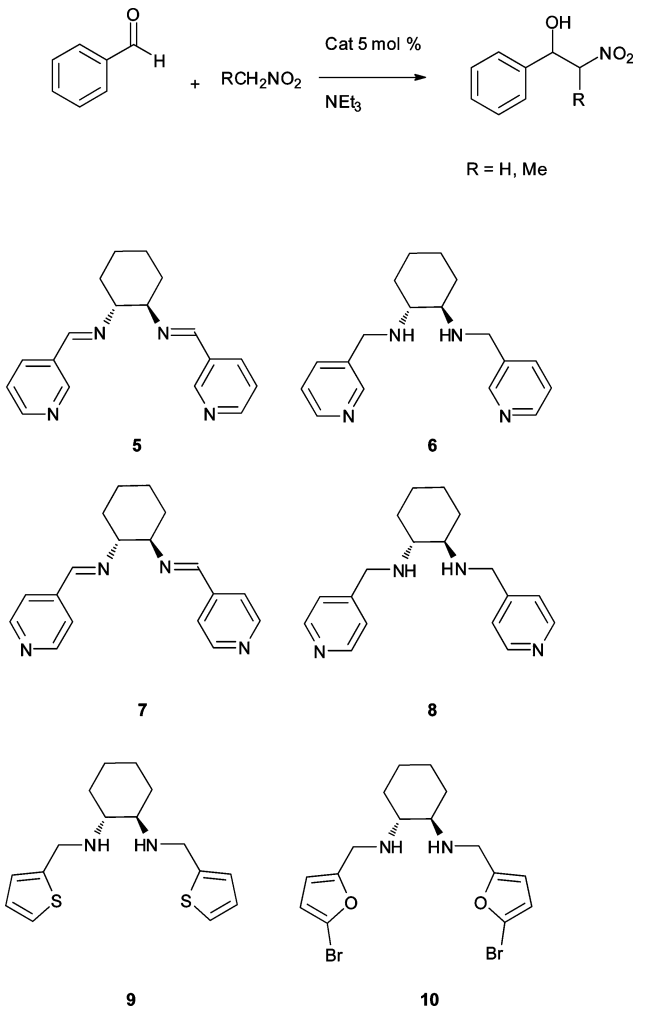
Catalyst prepared from[b]	Solvent	*T*/°C	Con/%[c]	Anti:Syn[d]	ee[d]
L1	MeOH	20	80	59 : 41	33, 34
L1	MeOH	0	38	58 : 42	18, 21
L1	EtOH	20	31	60 : 40	10, 9
L1	IPA	20	61	62 : 38	11, 16
L2	MeOH	20	97	68 : 32	32, 25
L2	MeOH	0	86	79 : 21	52,12
L3	MeOH	20	73	61 : 36	13, 7
L4	MeOH	20	99	73 : 27	36, 41
L5	MeOH	20	99	58 : 42	10, 12
L6	MeOH	20	95	59 : 41	7, 38
L6	MeOH	0	72	33 : 67	46, 30
L7	MeOH	20	96	60 : 40	5, 18
L8	MeOH	20	95	41 : 59	10, 37
L9	MeOH	20	87	57 : 43	20, 50
L9	MeOH	0	77	30 : 70	46, 29
L10	MeOH	20	90	46 : 54	33, 8

[a] Catalyst:benzaldehyde:Nitroethane molar ratio employed was 0.05 : 1 : 10, [b] see Scheme 2 and 3; [c] conversion as determined by ^{1}H NMR spectroscopic analysis, [d] determined by chiral HPLC.

With nitromethane modest conversions and selectivities were achieved with Cu(II) complexes prepared from **L1–L4**. The highest ee was achieved with the furan system, **L9**. In most cases with nitroethane the *anti* form of the product was prevalent and modest ee's were achieved; the highest being 50% ee for the *syn* isomer with the Cu(II) complexes from **L9** and 52% for the *anti* isomer with $[Cu(\mathbf{2})]^{2+}$.

Conclusions

In summary a series of Cu(II) Schiff base complexes have been prepared and structurally characterised. The complexes have been shown to react with the solvent to generate an α-amino ether group. This should act as warning that in all cases when imines are complexed in alcohol solvents all may not be what is seems. The complexes, and related ligand systems, were tested for the Henry reaction.



Scheme 3 Top: Henry reaction studied in this work. Bottom: extra ligands employed for comparison.

Experimental

^{1}H and ^{13}C{^{1}H}are NMR spectra were recorded on a Bruker 300 or 250 MHz spectrometer, and referenced to residual solvent peaks ($CDCl_3$). Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. (1*R*,2*R*)-1,2-diaminocyclohexane was resolved from the commercially available *trans*-1,2-diaminocyclohexane by the method of Jacobson.

Metal complexes

$Cu(OTf)_2$ (0.20 g, 0.55 mmol) was dissolved in methanol (30 ml) under argon, and **L1** (0.16 g, 0.55 mmol) added. The reaction mixture was stirred for 72 h at room temperature before the solvent was removed by rotary evaporation. The product was recrystallised from the minimum amount of methanol. Calcd. $C_{20.7}H_{22.8}N_4O_{6.70}F_6S_2Cu_1$ C, 36.75; H, 3.40; N, 8.28. Found C, 36.8; H, 3.33; N, 8.25. IR 2945 w, 2868 w (C–H), 1663 m (C═N), 1607 m, 1481 m, 1451 m (C═N, C═C pyridine), 1293 m, 1278 m, 1149 s, 1027 s, 784 m, 634 s. Analytical data for EtOH solvent preparation: Calcd. $C_{21.7}H_{25.1}N_4O_{6.85}F_6S_2Cu_1$ C, 37.60; H, 3.65; N, 8.08. Found C, 37.4; H, 3.56; N, 7.98. IR 2950 w, 1668 m (C═N), 1607 m,

Table 5 X-Ray crystallographic data

Cation	[Cu(**1**-MeOH)]$^{2+}$	[Cu(**1**-EtOH)]$^{2+}$	[Cu(**1**)]$^{2+}$	[Cu(**1**)]$^{2+}$	[Cu(**1**)]$^{2+}$
Solvent[a]	MeOH	EtOH	IPA	$MeO(CH_2)_2OH$	CF_3CH_2OH
Empirical formula	$C_{20.7}H_{22.8}CuF_6N_4O_{6.7}S_2$	$C_{21.7}H_{25.1}CuF_6N_4O_{6.85}S_2$	$C_{23}H_{28}CuF_6N_4O_7S_2$	$C_{21}H_{22.5}CuF_6N_4O_{6.5}S_2$	$C_{22}H_{21}CuF_9N_4O_7S_2$
Formula weight	676.49	693.22	714.15	676.59	752.09
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*1	*P*1	*P*1	*P*1	*P*1
a/Å	8.8600(5)	8.8420(3)	9.5699(3)	8.8900(2)	9.5450(8)
b/Å	11.2890(5)	11.6520(4)	11.4168(3)	11.4790(3)	11.4260(10)
c/Å	14.6510(7)	14.8430(5)	13.9033(4)	15.4820(5)	13.6980(12)
α (°)	80.751(3)	98.123(2)	76.376(2)	111.620(1)	78.636(6)
β (°)	86.603(2)	93.505(2)	82.061(1)	101.199(1)	83.184(5)
γ (°)	69.248(3)	111.186(2)	88.308(1)	93.665(1)	88.992(5)
Volume/Å^3	1352.51(12)	1401.10(8)	1462.14(7)	1424.80(7)	1454.3(2)
Z	2	2	2	2	2
D_{calc}/g cm^{-3}	1.661	1.643	1.622	1.577	1.718
μ/mm^{-1}	1.050	1.016	0.977	0.996	1.001
Refns collected	25918	18888	27768	26438	10765
θ range/°	3.57–27.48	4.20–27.48	3.54–27.49	3.56–27.47	4.16–24.16
Flack parameter	0.027(13)	0.017(15)	0.022(13)	0.02(2)	–0.05(2)
Indep. refns(R_{int})	11526, 0.0452	10538, 0.0570	12531, 0.0391	12251, 0.0496	7741, 0.0629
Goodness-of-fit	1.018	1.033	1.029	1.036	1.048
R_1, wR_2 [$I > 2\sigma(I)$]	0.0533, 0.1296	0.0575, 0.1340	0.0528, 0.1213	0.0585, 0.1375	0.0548, 0.1137
R_1, wR_2 [all data]	0.0815, 0.1481	0.0725, 0.1449	0.0754, 0.1343	0.0922, 0.1559	0.0869, 0.1313
Max, min difference/e Å^{-3}	0.681, –0.600	0.736, –0.822	1.459, –0.518	1.219, –0.504	0.419, –0.447

Cation	[Cu(**1**)]$^{2+}$	[Cu(**1**)]$^{2+}$	[Cu(**2**)]$^{2+}$	[Cu(**3**·MeOH)]$^{2+}$
Solvent[a]	$C_6H_5CH(OH)CH_3$	MeOH+AcOH	MeOH	MeOH
Empirical formula	$C_{36}H_{40}CuF_6N_4O_8S_2$	$C_{21}H_{24}CuF_6N_4O_7S_2$	$C_{20}H_{24}CuF_6N_4O_6S_2$	$C_{23}H_{28}CuF_6N_4O_7S_2$
Formula weight	898.38	686.10	658.09	714.15
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic
Space group	$P4_32_12$	*P*1	$P2_1$	*P*1
a/Å	21.106(5)	8.8590(2)	9.5520(2)	9.6290(3)
b/Å	21.106(5)	11.2530(3)	27.0250(10)	11.7880(5)
c/Å	8.547(3)	14.7790(5)	10.1510(4)	13.8240(5)
α (°)	90	80.180(1)	90	99.918(2)
β (°)	90	86.856(1)	97.143(2)	105.773(2)
γ (°)	90	68.960(1)	90	96.220(1)
Volume/Å^3	3807.5(16)	1354.92(7)	2600.07(15)	1467.40(9)
Z	4	2	4	2
D_{calc}/g cm^{-3}	1.567	1.682	1.681	1.616
μ/mm^{-1}	0.770	1.050	1.088	0.973
Refns collected	37331	19858	34132	29086
θ range/°	2.65–26.74	3.83–27.46	3.86–27.50	3.56–27.55
Flack parameter	0.101(14)	–0.025(10)	–0.005(9)	0.004(8)
Indep. refns (R_{int})	4433, 0.0419	10511, 0.0355	11316, 0.0568	12630, 0.0335
Goodness-of-fit	1.139	1.023	1.039	1.042
R_1, wR_2 [$I > 2\sigma(I)$]	0.0413, 0.0940	0.0416, 0.1024	0.0462, 0.1061	0.0341, 0.0774
R_1, wR_2 [all data]	0.0435, 0.0958	0.0490, 0.1080	0.0711, 0.1061	0.0438, 0.0830
Max, min difference/e Å^{-3}	0.280, –0.484	0.600, –0.566	0.401, –0.665	0.302, –0.521

[a] Solvent used for the recrystallisation, see Scheme 2 for further details.

1482 m, 1450 m (C═N, C═C pyridine), 1293 m, 1278 m, 1239, 1143 s, 1027 s, 773 m, 630 s. Analytical data for IPA solvent preparation $C_{20}H_{20}N_4O_6F_6S_2Cu_1$ C, 36.73; H, 3.08; N, 8.57. Found C, 36.5; H, 2.81; N, 8.50. IR 2945 w, 2869 w (C–H), 1663 m (C═N), 1607 m, 1481 m, 1451 m (C═N, C═C pyridine), 1293 m, 1239 s, 1278 m, 1149 s, 1027 s, 784 m, 634 s.

X-Ray crystallography†

All data were collected on a Nonius Kappa CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 150(2) K except 1-$C_6H_5CH(OH)CH_3$ which were recorded at station I19 Diamond light source using Synchrotron radiation (λ = 0.68890 Å), due to their small size {0.03 × 0.03 × 0.07 mm}. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs, see Table 5 for full crystallographic parameters.[17] Hydrogen atoms were included in idealised positions and refined using the riding model, except for an OH group in [Cu(**3**·MeOH)]$^{2+}$. Refinements were generally straightforward with the following exceptions and points of note. In [Cu(**1**)]$^{2+}$ crystallised in IPA one molecule of solvent was disordered over two positions in a 75 : 25 ratio and refined isotropically. For the complexes recrystallised in CF_3CH_2OH and 1-phenyl ethanol the hydrogens of the alcohol OH group were placed in calculated positions. For Cu(**3**·MeOH)$(CF_3SO_3)_2$ the alcohol hydrogen was found from analysis of the final difference Fourier map and freely refined. For the complex crystallised in 1-phenyl ethanol the solvent of crystallisation was 75% *S* enantiomer and 25% *R*. As the compounds contain optically pure (1*R*,2*R*)-diaminocyclohexane moieties, PLATON checks suggesting the

approximate presence of inversion centres in these structures can immediately be disregarded.

Typical catalytic procedure

Under nitrogen the solvent (10 ml) was added to a Schlenk flask, to this the Cu(II) catalyst was added (0.05 mmol) and the solution stirred. Benzaldehyde (0.1 ml, 1 mmol), nitromethane (0.55 ml, 10 mmol) and NEt_3 (35 μl, 0.25 mmol) were added and the solution stirred for the appropriate amount of time. After the desired time the reaction was filtered through a plug of silica and the solvents were removed in vacuo. ^{1}H NMR spectroscopy was used to determine the conversion by analysis of the 1H integral for the PhC**H**O of benzaldehyde at 9.94 ppm to the 1H integral of PhC**H**(OH)CH_2NO_2 at 5.45 ppm. The enantiomeric excess was determined by HPLC using an Agilent Compact 1120 LC with UV detection (230 nm). A flow rate of IPA:hexane (1 : 9) at 1 ml min^{-1} was used with a OD-H column, the retention times were 16.6 and 20.5 min for the two enantiomers. For nitroethane two doublets at 5.40 ppm (*anti*) and 5.00 ppm (*syn*) were observed. In the HPLC (OD-H, 2 : 98 IPA/hexane at 1 ml min^{-1}, UV = 210 nm) four peaks at 34.3, 52.4 for the *anti* isomer and 44.4 and 56.7 for the *syn* isomer were observed.

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