

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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Supporting Experimental Data:

A number of pyridine-containing Jacobsen-type ligands have been prepared from chirally resolved 1,2-diaminocyclohexane. The procedures implemented were taken from the literature.

Synthesis of (R,R)-1,2-diaminocyclohexane tartrate salt: L-(+)-tartaric acid (150g, 1.0 mol) was dissolved in distilled water (400 ml) and a mixture of cis/trans 1,2-diaminocyclohexane added (240 ml, 2.0 mol) so that the reaction temperature reached 70 °C. To this glacial acetic acid was added (100 ml, 1.8 mol) so that the reaction temperature reached 90 °C. The resulting slurry was stirred for a further 2 h, and then cooled to 5 °C for 2 h. The resulting precipitate was collected by vacuum filtration and washed with 5 °C distilled water (2 × 50 ml) and then methanol (5 × 100 ml). The crude product was then recrystallised by dissolving the compound in distilled water at 90 °C and leaving to cool to room temperature overnight. The purified product was collected by vacuum filtration and dried under reduced pressure.

¹H (D₂O) 1.39 (m, 4H), 1.79 (m, 2H), 2.13 (m, 2H), 3.33 (m, 2H, CHNH₃⁺), 4.29 (s, 2H, CHOH). ¹³C{H} (D₂O) 23.2 (CH₂), 29.8 (CH₂), 52.5 (CH), 74.3 (CHOH), 178.9 (COOH). Mass spec: HR-ESI Calc for [M⁺] 115.1235 found 115.1241

Synthesis of (R,R)-1,2-diaminocyclohexane: (R,R)-1,2-diaminocyclohexane tartrate salt (26.4 g, 100 mmol) was dissolved in 80 ml distilled water and 100 ml CH₂Cl₂. To this a cooled solution of sodium hydroxide (9.6 g in 80 ml distilled water, 3 mol dm⁻³) was added dropwise. Sodium chloride was added (6 g, 103 mmol), and then the reaction mixture was stirred for 30 minutes. Following this the aqueous phase was decanted and extracted with chloroform (3 × 20 ml), with the combined organic layers being dried over magnesium sulphate. The mixture was filtered and the solvent removed by rotary evaporation. The product was dried under reduced pressure and stored at -20 °C.

¹H (CDCl₃) 1.04 (m, 2H), 1.19 (m, 2H), 1.60 (m, 2H), 1.76 (m, 2H), 2.18 (m, 2H). ¹³C{H} (CDCl₃) 25.8 (CH₂), 35.9 (CH₂), 58.1 (CH). Mass spec: HR-ESI Calc for [M⁺] 115.1235 found 115.1243.

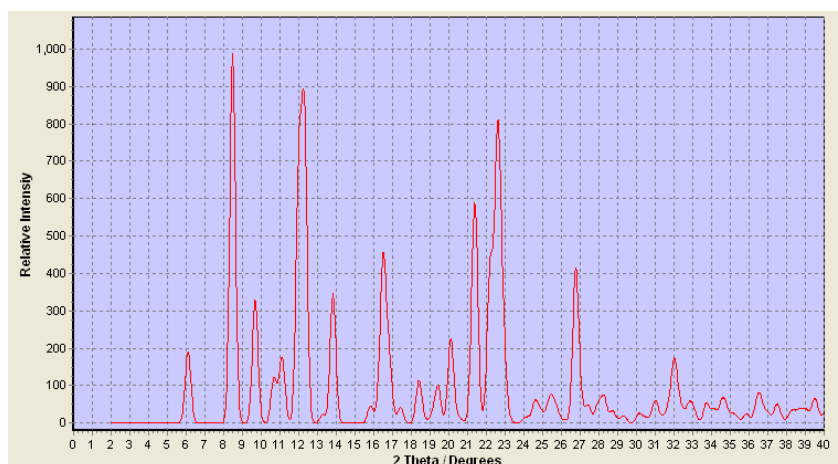
Ligand 1:

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 2-pyridinecarboxaldehyde (0.84 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, before the solvent was removed by rotary evaporation. The product was dried under reduced pressure. Yield 91%.

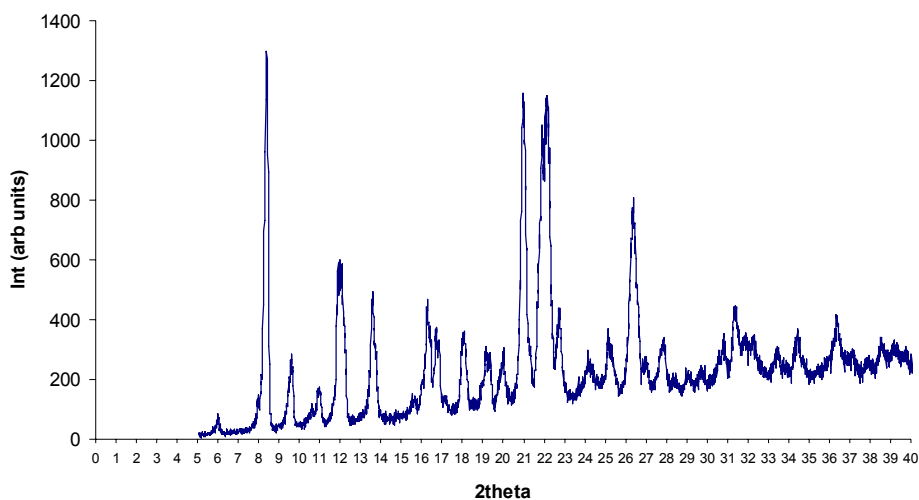
^1H (CDCl_3) 1.49 (m, 2H), 1.83 (m, 6H), 3.53 (m, 2H, CHN cyclohexane), 7.18 (m, 2H), 7.58 (t, 2H), 7.84 (d, 2H), 8.29 (s, 2H CHN imine), 8.52 (d, 2H). $^{13}\text{C}\{\text{H}\}$ (CDCl_3) 24.4 (CH_2), 32.7 (CH_2), 73.6 (CHN cyclohexane), 121.3 (CH), 124.5 (CH), 136.4 (CH), 149.2 (CHN Ar), 154.6 (C Ar), 161.5 (CHN imine). Mass spec: HR-ESI Calc for $[\text{M}^+]$ 293.1766 found 293.1757.

See full paper for Cu(II) complexes

pXRD for $\text{Cu}(\text{I-MeOH})(\text{CF}_3\text{SO}_3)_2$

Calculated:

pXRD of the crude product before recrystallisation: ($\text{CuK}\alpha$ X-rays, on a Philips PW1710)



Ligand 2

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 2-pyridinecarboxaldehyde (0.84 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, upon which sodium borohydride was added (0.5 g, 13.2 mmol). Following a further 3h reaction time, the solvent was removed by rotary evaporation and a 50:50 water:dichloromethane mix was added to the product. The organic layer was decanted off, and the remaining aqueous layer washed twice more with dichloromethane. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed by rotary evaporation before the product was dried under reduced pressure.

^1H (CDCl₃) 1.04 (m, 2H), 1.20 (m, 2H), 1.69 (m, 2H), 2.11 (m, 2H), 2.27 (m, 2H), 3.81 (d J = 14 Hz, 2H, CH₂NH), 3.99 (d J = 14 Hz, 2H, CH₂NH), 7.11 (m, 2H), 7.47 (d, 2H), 7.70 (t, 2H), 8.55 (d, 2H). $^{13}\text{C}\{\text{H}\}$ (CDCl₃) 24.0 (CH₂), 30.9 (CH₂), 53.2 (CH₂NH amine), 60.3 (CHN cyclohexane), 120.8 (CH), 135.4 (CH), 148.0 (CHN Ar), 159.5 (C Ar). Mass spec: HR-ESI Calc for [M⁺] 297.2079 found 297.2068.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.16 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. The complex was recrystallised in the minimum amount of methanol and 1 cm³ of diethyl ether. Crystals were formed at -20°C after 48 hrs. Mass spec: HR-ESI Calc for [M⁺] 508.0817 found 508.0798. Elemental analysis: calc C, 36.5; H, 3.68; N, 8.51 found C, 36.6; H, 3.70; N, 8.60, IR 2937 w, 1615 m, 1447 m, 1287 s, 1236 s, 1220 s, 1155 s, 1026 s, 893 m, 769 s.

Ligand 3

(*R,R*)-1,2-diaminocyclohexane (0.15 g, 1.3 mmol) was dissolved in 20 ml methanol, and 3-methylpyridine-2-carboxaldehyde (0.3 ml, 2.6 mmol) added. The reaction mixture was stirred for 24h at room temperature. Following this the mixture was filtered and the solvent of the filtrate removed by rotary evaporation. The product was dried under reduced pressure.

^1H (CDCl₃) 1.45 (m, 2H), 1.79 (m, 6H), 2.31 (s, 6H), 3.46 (m, 2H), 7.02 (m, 2H), 7.32 (m, 2H), 8.4 (d, 2H, CHN Ar) 8.42 (s, 2H, CHN imine). $^{13}\text{C}\{\text{H}\}$ (CDCl₃) 20.0 (CH₃), 24.2

(CH₂), 32.9 (CH₂), 74.9 (CHN cyclohexane), 123.9 (CH Ar), 133.5 (C, Ar), 139.5 (CH Ar), 147.5 (CHN imine), 152.1 (C), 161.5 (CHN imine). Mass spec: HR-ESI Calc for [M⁺] 321.2079 found 321.2076.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.18 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. The complex was recrystallised in the minimum amount of methanol and 1 cm³ of diethyl ether. Crystals were formed after 48 hrs at -20°C. Mass spec: HR-ESI Calc for [M⁺] 532.0817 found 532.0767. Elemental analysis C₂₂H₂₄N₄O₆F₆S₂Cu₁ : calc C, 38.7; H, 3.54; N, 8.21 found C, 37.8; H, 3.70; N, 8.17. IR 2945 w, 1656 m, 1593 m, 1462 m, 1344 m, 1274 m, 1240 s, 1158 s, 1028 m, 812 s 750 m.

Ligand 4

(*R,R*)-1,2-diaminocyclohexane (0.3 g, 2.6 mmol) was dissolved in 30 ml methanol, and 3-methylpyridine-2-carboxaldehyde (0.60 ml, 5.2 mmol) added. The reaction mixture was stirred for 3h at room temperature, upon which sodium borohydride was added (0.3 g, 7.9 mmol). Following a further 3h reaction time, the solvent was removed by rotary evaporation and a 50:50 water:dichloromethane mix was added to the product. The organic layer was decanted off, and the remaining aqueous layer washed twice more with dichloromethane. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed by rotary evaporation before the product was dried under reduced pressure.

¹H (CDCl₃) 1.17 (m, 2H), 1.67 (m, 2H), 2.32 (s, 6H, Me), 2.35 (br m, 6H), 3.78 (d J = 14 Hz, 2H, CH₂NH), 4.04 (d J = 14 Hz, 2H, CH₂NH), 7.06 (m, 2H), 7.25 (m, 2H), 7.38 (m, 2H), 8.33 (m, 2H). ¹³C{H} (CDCl₃) 18.1 (CH₃), 25.0 (CH₂), 31.6 (CH₂), 121.8 (CH Ar), 131.3 (C, Ar), 137.6 (CH Ar), 146.2 (CH Ar). Mass spec: HR-ESI Calc for [M⁺] 325.2392 found 325.2376

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.18 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced

pressure. Mass spec: HR-ESI Calc for $[M^+]$ 536.1130 found 536.1307. IR 2938 w, 2865 w, 1598 m, 1461 m, 1273 m, 1230 s, 1156 s, 1024 s, 955 s, 802 m.

Ligand 5

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 3-pyridinecarboxaldehyde (0.83 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, before the solvent was removed by rotary evaporation. The product was dried under reduced pressure.

^1H (CDCl_3) 1.44 (m, 2H), 1.81 (m, 6H), 3.39 (m, 2H, CHN cyclohexane), 7.19 (m, 2H), 7.91 (m, 2H, CH Ar), 8.17 (s, 2H, CHN imine), 8.49 (d, 2H, CHCHN Ar), 8.69 (s, 2H, CCHN Ar). $^{13}\text{C}\{\text{H}\}$ (CDCl_3) 24.3 (CH_2), 32.7 (CH_2), 74.1 (CHN cyclohexane), 123.5 (CH), 131.7 (C), 134.4 (CH), 149.9 (CHN Ar), 151.3 (CHN Ar), 158.0 (CHN imine). Mass spec: HR-ESI Calc for $[M^+]$ 293.1766 found 293.1774.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.16 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_6\text{F}_6\text{S}_2\text{Cu}_1$ C, 36.73; H, 3.08; N, 8.57. Found C, 35.8; H, 3.22; N, 8.10. IR 2945 w, 1664 (m), 1606 m, 1479 m, 1451 m, 1279 m, 1241 s, 1222 m, 1027 s, 775 m.

Ligand 6

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 3-pyridinecarboxaldehyde (0.83 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, upon which sodium borohydride was added (0.5 g, 13.2 mmol). Following a further 3h reaction time, the solvent was removed by rotary evaporation and a 50:50 water:dichloromethane mix was added to the product. The organic layer was decanted off, and the remaining aqueous layer washed twice more with dichloromethane. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed by rotary evaporation before the product was dried under reduced pressure.

^1H (CDCl_3) 1.02 (m, 2H), 1.16 (m, 2H), 1.67 (m, 2H), 2.14 (m, 6H), 3.62 (d $J = 13.5$ Hz, 2H, CH_2NH), 3.86 (d $J = 13.5$ Hz, 2H, CH_2NH), 7.19 (m, 2H), 7.58 (m, 2H), 8.46 (m, 4H). $^{13}\text{C}\{\text{H}\}$ (CDCl_3) 24.9 (CH_2), 31.5 (CH_2), 48.3 (CH_2NH amine), 61.0 (CHN cyclohexane),

123.4 (CH), 135.7 (CH), 136.23 (C), 148.4 (CH) 149.6 (CH). Mass spec: HR-ESI Calc for $[M^+]$ 297.2079 found 297.2055.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.163 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. Elemental analysis: calc $C_{20}H_{24}N_4O_6F_6S_2Cu_1$ C, 36.5; H, 3.68; N, 8.51 found C, 36.0; H, 3.29; N, 8.90. IR 2928 w, 1611 (m), 1439 m, 1230 s, 1222 m, 1160 m, 1024 m, 802 m, 707 s.

Ligand 7

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 4-pyridinecarboxaldehyde (0.83 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, before the solvent was removed by rotary evaporation. The product was dried under reduced pressure.

1H ($CDCl_3$) 1.36 (m, 2H), 1.73 (m, 6H), 3.32 (m, 2H), 7.32 (d, 4H), 8.03 (s, 2H, CHN imine), 8.46 (d, 4H, CHN Ar). $^{13}C\{H\}$ ($CDCl_3$) 24.2 (CH_2), 32.6 (CH_2), 73.8 (CHN cyclohexane), 120.4 (CH), 142.9 (C), 150.3 (CHN Ar), 159.1 (CHN imine). Mass spec: HR-ESI Calc for $[M^+]$ 293.1766 found 293.1770.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.16 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. $C_{20}H_{20}N_4O_6F_6S_2Cu_1$ C, 36.73; H, 3.08; N, 8.57. Found C, 36.1; H, 3.21; N, 8.01. IR 2945 w, 1663 m, 1606 m, 1479, 1439 m, 1451, 1279 m, 1242 m, 1222 m, 1144 s, 1027 s, 775 s.

Ligand 8

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 2-pyridinecarboxaldehyde (0.83 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, upon which sodium borohydride was added (0.5 g, 13.2 mmol). Following a further 3h reaction time, the solvent was removed by rotary evaporation and a

50:50 water:dichloromethane mix was added to the product. The organic layer was decanted off, and the remaining aqueous layer washed twice more with dichloromethane. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed by rotary evaporation before the product was dried under reduced pressure. ^1H (CDCl_3) 0.97 (m, 2H), 1.15 (m, 2H), 1.66 (m, 2H), 2.10 (m, 4H), 3.65 (d $J = 14.5$ Hz, 2H, CH_2NH), 3.88 (d $J = 14.5$ Hz, 2H, CH_2NH), 7.19 (m, 4H), 8.47 (m, 4H). $^{13}\text{C}\{\text{H}\}$ (CDCl_3) 23.8 (CH_2), 30.4 (CH_2), 53.1 (CH_2NH amine), 60.1 (CHN cyclohexane), 121.9 (CH Ar), 148.8 (CHN Ar), 149.1 (C Ar). Mass spec: HR-ESI Calc for $[\text{M}^+]$ 297.2079 found 297.2034

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.163 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. Elemental analysis: calc $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_6\text{F}_6\text{S}_2\text{Cu}_1$ C, 36.5; H, 3.68; N, 8.51 found C, 36.6; H, 3.70; N, 8.60. IR 2961 w, 1622 m, 1444 m, 1429 m, 1240, 1252 m, 1161, 1023 s, 796 s.

Ligand 9

(*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 2-thiophenecarboxaldehyde (0.83 ml, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, upon which sodium borohydride was added (0.5 g, 13.2 mmol). Following a further 3h reaction time, the solvent was removed by rotary evaporation and a 50:50 water:dichloromethane mix was added to the product. The organic layer was decanted off, and the remaining aqueous layer washed twice more with dichloromethane. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed by rotary evaporation before the product was dried under reduced pressure.

^1H (CDCl_3) 1.01 (m, 2H), 1.22 (m, 2H), 1.71 (m, 2H), 2.11 (m, 2H), 2.28 (m, 2H), 3.84 (d $J = 14$ Hz, 2H, CH_2NH amine), 4.08 (d $J = 14$ Hz, 2H, CH_2NH amine), 6.93 (m, 4H), 7.18 (m, 2H). $^{13}\text{C}\{\text{H}\}$ (CDCl_3) 25.0 (CH_2), 31.4 (CH_2), 45.4 (CH_2NH amine), 60.3 (CHN cyclohexane), 124.2 (CH Ar), 124.4 (CH Ar), 126.6 (CHS Ar), 145.0 (CS Ar). Mass spec: HR-ESI Calc for $[\text{M}^+]$ 307.1303 found 307.1311.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.17 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. Elemental analysis: calc C₁₈H₂₂N₂O₆F₆S₄Cu₁ C, 32.4; H, 3.32; N, 4.19 found C, 32.8; H, 3.33; N, 4.80. IR 2938 w, 1598 m, 1462 m, 1274 s, 1233 s, 1156 s, 1024 s, 956 m, 802 s, 723 m.

Ligand 10

R,R-1,2-diaminocyclohexane (0.5 g, 4.4 mmol) was dissolved in 40 ml methanol, and 5-bromo-2-furaldehyde (1.5 g, 8.8 mmol) added. The reaction mixture was stirred for 3h at room temperature, upon which sodium borohydride was added (0.5 g, 13.2 mmol). Following a further 3h reaction time, the solvent was removed by rotary evaporation and a 50:50 water:dichloromethane mix was added to the product. The organic layer was decanted off, and the remaining aqueous layer washed twice more with dichloromethane. The organic layers were combined and dried over magnesium sulphate. The solvent was then removed by rotary evaporation before the product was dried under reduced pressure. ¹H (CDCl₃) 1.00 (m, 2H), 1.20 (m, 2H), 1.66 (m, 2H), 1.97 (m, 2H), 2.16 (m, 2H), 3.59 (d J = 14.5 Hz, 2H, CH₂NH amine), 3.76 (d J = 14.5 Hz, 2H, CH₂NH amine), 6.12 (d J = 3 Hz, 2H, Ar), 6.17 (d J = 3 Hz, 2H, Ar). ¹³C{¹H} (CDCl₃) 24.9 (CH₂), 31.4 (CH₂), 43.6 (CH₂NH amine), 59.1 (CHN cyclohexane), 109.9 (CH Ar), 111.8 (CH Ar), 120.2 (C Ar), 156.8 (CBr Ar). Mass spec: HR-ESI Calc for [M⁺] 432.9950 found 432.9964.

Copper(II) triflate (0.2 g, 0.55 mmol) was placed into a round bottom flask with a sidearm under argon. To this, the previously prepared ligand (0.17 g, 0.55 mmol) was added in methanol (30 ml), and the resulting mixture stirred at room temperature for 1h. Following this, the solvent was removed by rotary evaporation and the complex dried under reduced pressure. Mass spec: HR-ESI Calc for [M⁺] 644.8688 found 644.8673. IR 2925 m, 2853 m, 1505 m, 1448 m, 1338, 1119 m, 1009 s, 920 s, 777 m.

Summary of Energetic Data for Copper complexes

Computational Methods. All calculations were performed using the B3LYP¹ hybrid density functional under the Gaussian 03 package.² The spin unrestricted (UB3LYP) formalism was used throughout, except in the calculation of orbitals for visualization, where the Restricted Open-shell formalism (ROB3LYP) was used. Geometry optimisations were performed using a quasi-relativistic pseudopotential and associated basis set (SDD) for copper,³ and a 6-31G(d)⁴ basis set for all other atoms. Frequency calculations were performed at the optimised geometries to confirm the nature of the stationary points. Single point energies ('tight' convergence criteria) were calculated at the optimised geometries using the SDD basis set augmented with two f-polarisation functions⁵ for copper and the 6-311G(2d,p)⁶ basis set for all other atoms. Quoted values of ΔH and ΔG were obtained by taking the thermodynamic correction terms from the 6-31G(d) frequency calculation in combination with the electronic energies from the 6-311G(2d,p) calculation. Molecular orbitals were visualised using the Molekel program package.⁷

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- (2) M. J. Frisch *et al.*, Gaussian 09, Revision A.02., Gaussian, Inc., Wallingford CT, 2009.
- (3) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866-872.
- (4) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724-728. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654-3665. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.
- (5) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408-3420.
- (6) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650-654. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639-5648.
- (7) MOLEKEL 5.4, Varetto, U. Swiss National Supercomputing Centre: Manno (Switzerland).

All energies are relative to the Imine compound and the appropriate alcohol (H₂ for the amine).

Amine:

$\Delta E = -300.4$ kJ/mol
 $\Delta H = -237.2$ kJ/mol
 $\Delta G = -155.8$ kJ/mol

Imine:

$\Delta E = 0.0$ kJ/mol
 $\Delta H = 0.0$ kJ/mol
 $\Delta G = 0.0$ kJ/mol

Imine-Hydroxy:

$\Delta E = -81.8$ kJ/mol
 $\Delta H = -65.6$ kJ/mol
 $\Delta G = -14.6$ kJ/mol

Imine-Methoxy:

$\Delta E = -86.7$ kJ/mol
 $\Delta H = -73.1$ kJ/mol
 $\Delta G = -11.3$ kJ/mol

Imine-Methoxy (other diastereoisomer):

$\Delta E = -62.7$ kJ/mol
 $\Delta H = -50.0$ kJ/mol
 $\Delta G = +11.6$ kJ/mol

Imine-DiMethoxy:

$\Delta E = -152.5$ kJ/mol
 $\Delta H = -126.1$ kJ/mol
 $\Delta G = -15.9$ kJ/mol *ie. only -4.6 kJ/mol for addition of second MeOH*

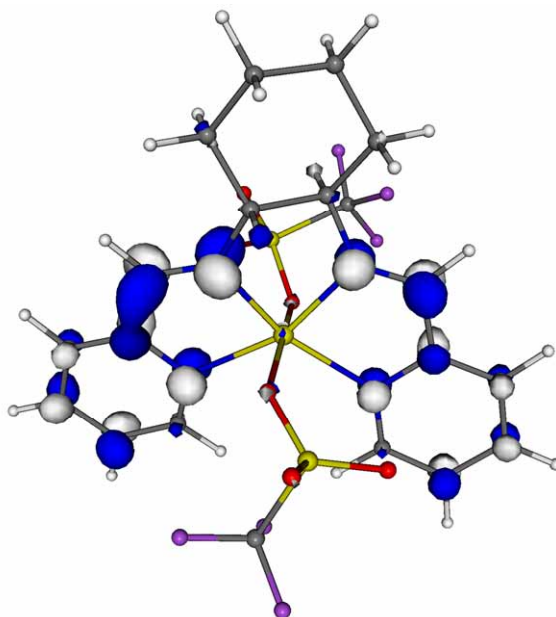
Imine-Ethoxy:

$\Delta E = -69.8$ kJ/mol
 $\Delta H = -56.2$ kJ/mol
 $\Delta G = +0.6$ kJ/mol

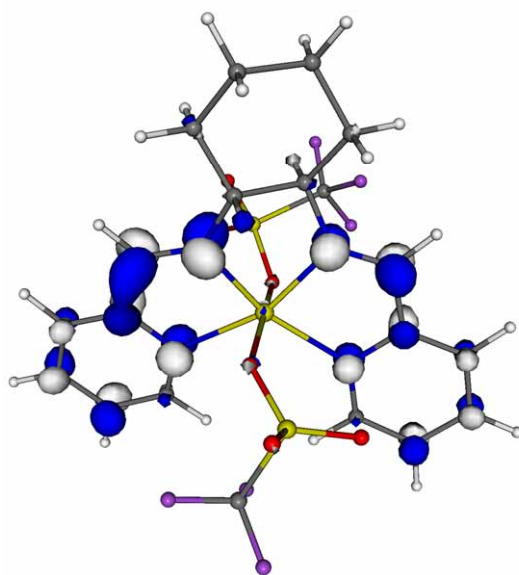
Imine-Propoxy:

$\Delta E = -62.2$ kJ/mol
 $\Delta H = -48.7$ kJ/mol
 $\Delta G = +9.8$ kJ/mol

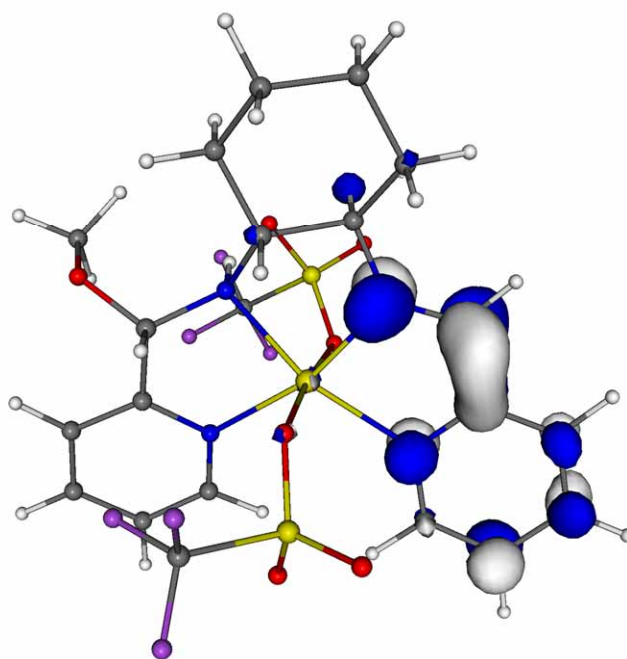
As can be seen, the addition of the first methanol is quite favourable, the addition of the second methanol also favourable, but less so. The addition of ethanol is energetically neutral (the reaction should proceed if excess ethanol present), but the addition of isopropanol is unfavourable. The other methanol isomer is much higher in energy (+22.9 kJ/mol).



Imine LUMO1 Cu(1-MeOH)(CF₃SO₃)₂



Imine LUMO $\text{Cu}(\mathbf{1}\text{-MeOH})(\text{CF}_3\text{SO}_3)_2$



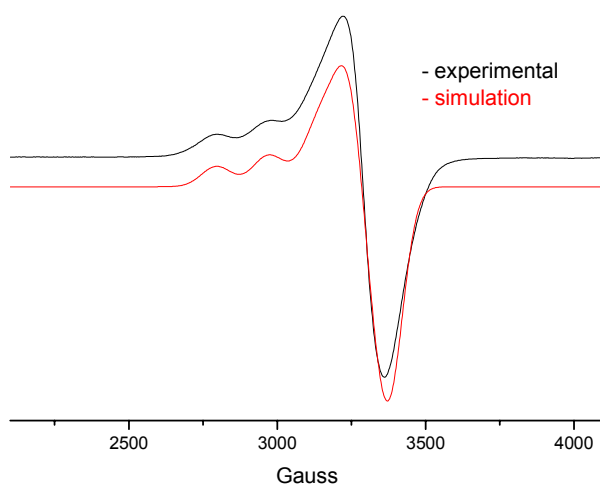
Imine-OMe LUMO $\text{Cu}(\mathbf{1}\text{-MeOH})(\text{CF}_3\text{SO}_3)_2$

EPR Analysis

Sample $\text{Cu}(\text{3})(\text{OTf})_2$

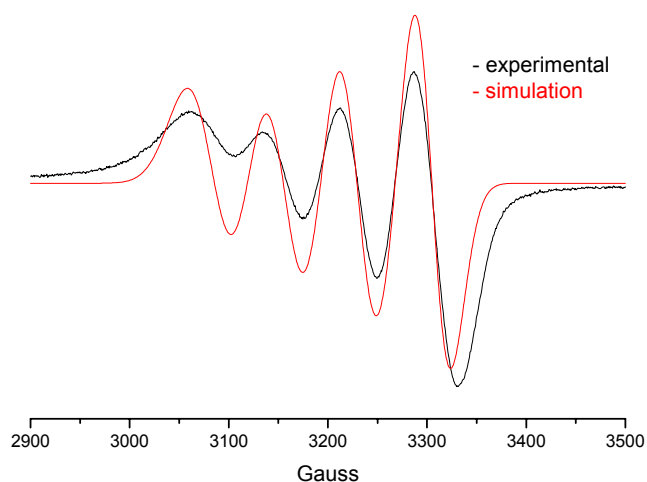
The simulation of the powder spectrum of sample $\text{Cu}(\text{3})(\text{OTf})_2$ at X-band, at 290 K and 100 K, is consistent with the presence of a Cu(II) complex with axial g and A values. It has $g_{\perp} = 2.052$, $g_{\parallel} = 2.208$ and $A_{\perp} = 10$ Gauss, $A_{\parallel} = 173$ Gauss.

Powder spectrum of $\text{Cu}(\text{3})(\text{OTf})_2$ at X-band (9.43 GHz) and at 290 K



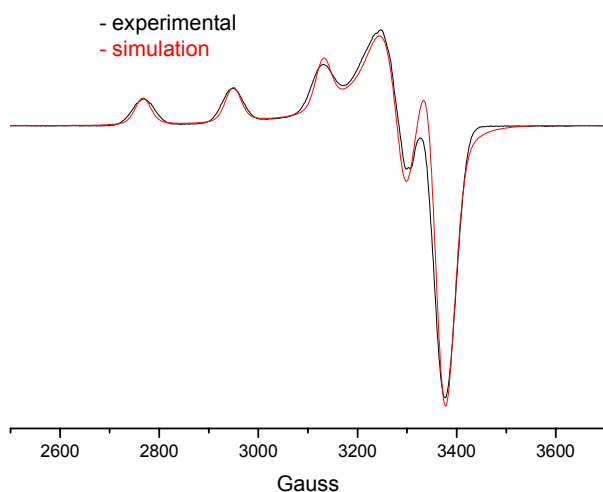
The sample $\text{Cu}(\text{3})(\text{OTf})_2$ was dissolved in MeOH with a drop of CH_2Cl_2 to help the formation of a glass. The fluid solution spectrum at X-band and 290 K shows the four lines due to the coupling with $\text{Cu}^{63/65}$ ($I = 3/2$) but it is not possible to simulate the superhyperfine with the nitrogen atoms because the spectrum is too broad. The simulation gives $g_{\text{iso}} = 2.108$, ($\text{Cu}^{63/65}$) $A_{\text{iso}} = 73.5$ Gauss.

Fluid solution spectrum of $\text{Cu}(\text{3})(\text{OTf})_2$ at X-band (9.43 GHz) in MeOH/dcm and at 290 K



The simulation of the frozen solution spectrum at X-band and 100 K gives an axial set of g values and A values with $g_{\perp} = 2.048$, $g_{\parallel} = 2.215$ and $A_{\perp} = 15$ Gauss, $A_{\parallel} = 182$ Gauss.

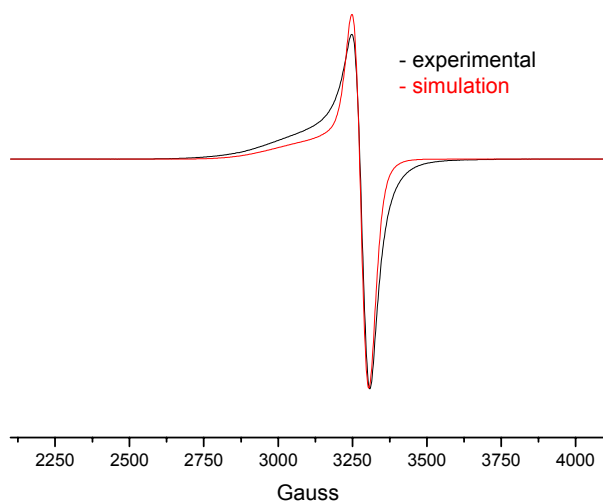
Frozen solution spectrum of **Cu(3)(OTf)₂** at X-band (9.43 GHz) in MeOH/dcm and at 290 K



Sample **Cu(1-MeOH)(CF₃SO₃)₂** in MeOH

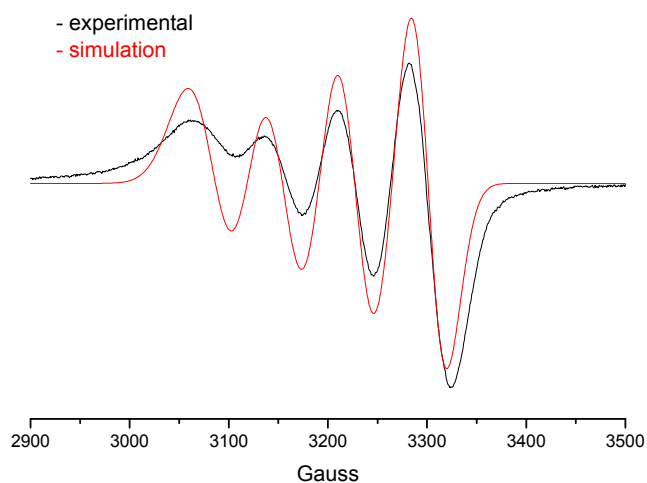
The simulation of the powder spectrum of sample **Cu(1-MeOH)(CF₃SO₃)₂** at X-band, at 290 K and 100 K, is consistent with the presence of a Cu(II) complex with axial g and A values. It has $g_{\perp} = 2.056$, $g_{\parallel} = 2.210$.

Powder spectrum of **Cu(1-MeOH)(CF₃SO₃)₂** at X-band (9.44 GHz) and at 290 K



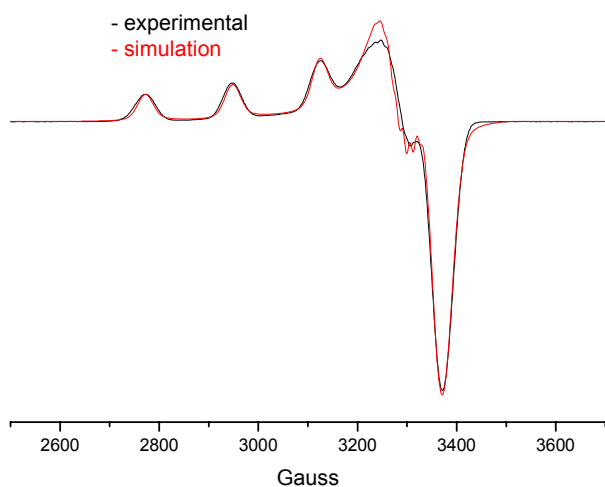
The sample $\text{Cu}(\mathbf{1}\text{-MeOH})(\text{CF}_3\text{SO}_3)_2$ was dissolved in MeOH with a drop of CH_2Cl_2 to help the formation of a glass. The fluid solution spectrum at X-band and 290 K shows the four lines due to the coupling with $\text{Cu}^{63/65}$ ($I = 3/2$) but it is not possible to simulate the superhyperfine with the nitrogen atoms. The simulation gives $g_{\text{iso}} = 2.108$, $(\text{Cu}^{63/65}) A_{\text{iso}} = 72.0$ Gauss.

Fluid solution spectrum of $\text{Cu}(\mathbf{1}\text{-MeOH})(\text{CF}_3\text{SO}_3)_2$ at X-band (9.42 GHz) in MeOH/dcm and at 290 K



The simulation of the frozen solution spectrum at X-band and 130 K gives an axial set of g values and A values with $g_{\perp} = 2.049$, $g_{\parallel} = 2.218$ and $A_{\perp} = 15$ Gauss, $A_{\parallel} = 176$ Gauss and it is possible to simulate the superhyperfine with four nitrogen atoms, which gives $(4 \times N^{14}) A_{\perp} = 13$ Gauss.

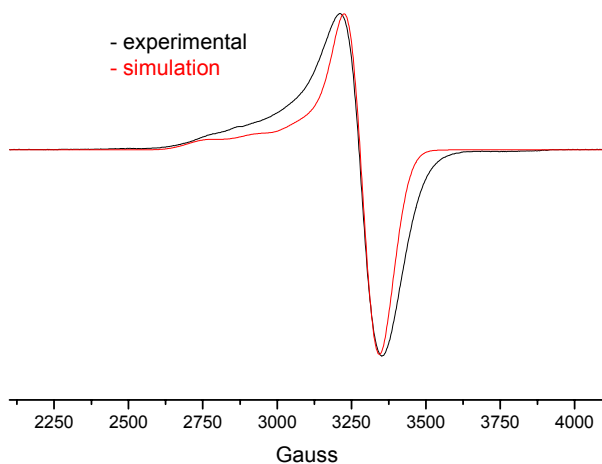
Frozen solution spectrum of $\text{Cu}(\mathbf{1}\text{-MeOH})(\text{CF}_3\text{SO}_3)_2$ at X-band (9.43 GHz) in MeOH/dcm and at 100 K



Sample Cu(1-EtOH)(CF₃SO₃)₂ in EtOH

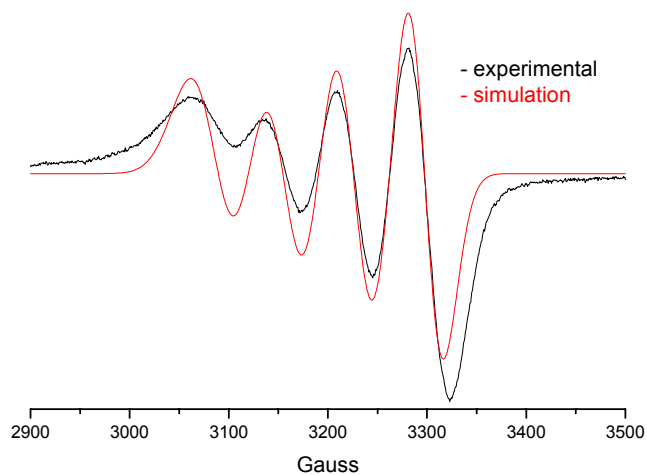
The simulation of the powder spectrum of sample Cu(1-EtOH)(CF₃SO₃)₂ at X-band, at 290 K and 100 K, is consistent with the presence of a Cu(II) complex with axial g and A values. It has $g_{\perp} = 2.052$, $g_{\parallel} = 2.248$. The spectrum is too broad to detect any Cu^{63/65} ($I = 3/2$) hyperfine.

Powder spectrum of Cu(1-EtOH)(CF₃SO₃)₂ at X-band (9.44 GHz) and at 290 K



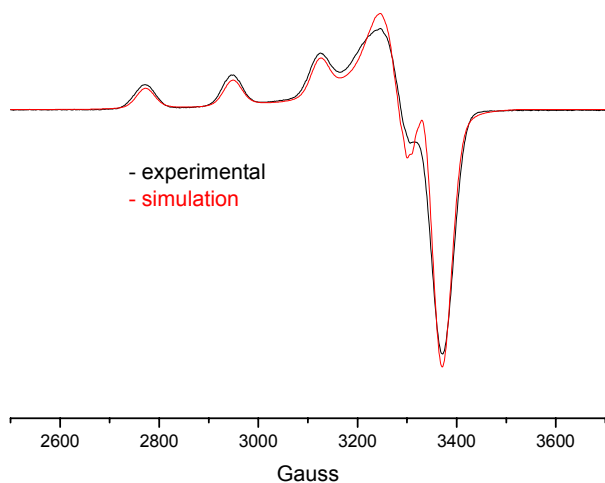
The sample Cu(1-EtOH)(CF₃SO₃)₂ was dissolved in EtOH with a drop of CH₂Cl₂ to help the formation of a glass. The fluid solution spectrum at X-band and 290 K shows the four lines due to the coupling with Cu^{63/65} ($I = 3/2$) but it is not possible to simulate the superhyperfine with the nitrogen atoms. The simulation gives $g_{\text{iso}} = 2.108$, (Cu^{63/65}) $A_{\text{iso}} = 70.0$ Gauss.

Fluid solution spectrum of Cu(1-EtOH)(CF₃SO₃)₂ at X-band (9.42 GHz) in EtOH/dcm and at 290 K



The simulation of the frozen solution spectrum at X-band and 100 K gives an axial set of g values and A values with $g_{\perp} = 2.049$, $g_{\parallel} = 2.218$ and $A_{\perp} = 15$ Gauss, $A_{\parallel} = 176$ Gauss and it is possible to simulate the superhyperfine with four nitrogen atoms, which gives ($4 \times N^{14}$) $A_{\perp} = 12$ Gauss.

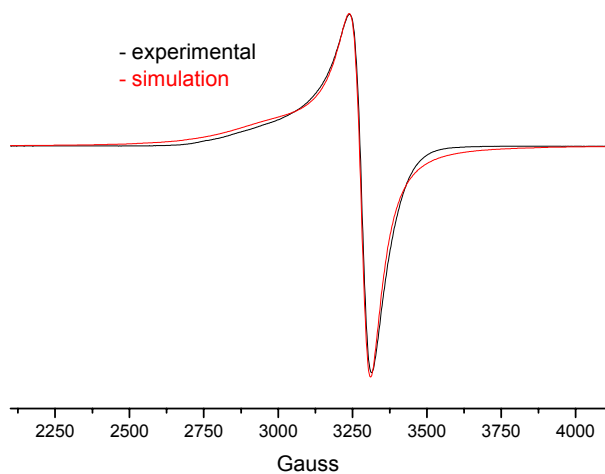
Frozen solution spectrum of $\text{Cu}(\text{1-EtOH})(\text{CF}_3\text{SO}_3)_2$ at X-band (9.42 GHz) in EtOH/dcm and at 100 K (3224x_6)



Sample $\text{Cu}(\text{1})(\text{OTf})_2$ in IPA

The simulation of the powder spectrum of sample $\text{Cu}(\text{1})(\text{OTf})_2$ at X-band, at 290 K and 100 K, is consistent with the presence of a Cu(II) complex with axial g and A values. It has $g_{\perp} = 2.054$, $g_{\parallel} = 2.285$.

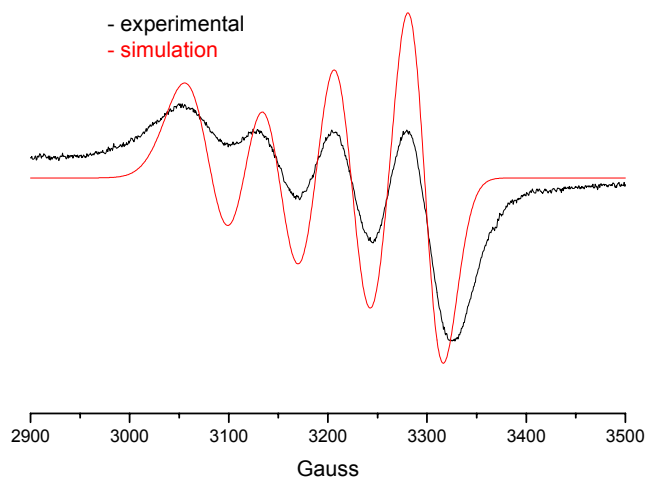
Powder spectrum of $\text{Cu}(\text{1})(\text{OTf})_2$ at X-band (9.44 GHz) and at 100 K



The sample $\text{Cu}(\text{1})(\text{OTf})_2$ was dissolved in iPrOH with a drop of CH_2Cl_2 to help the formation of a glass. The fluid solution spectrum at X-band and 290 K shows the four

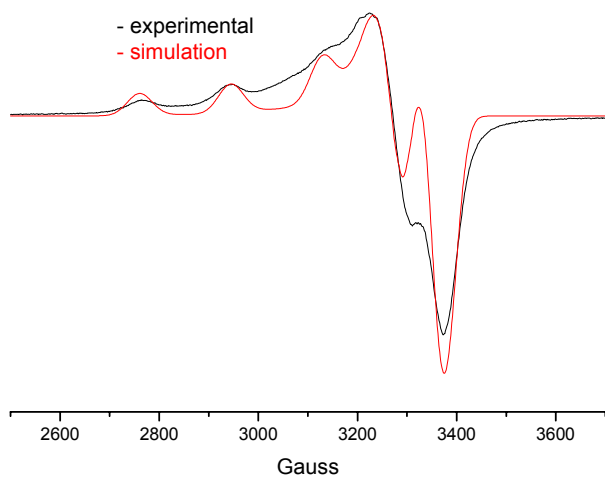
lines due to the coupling with $\text{Cu}^{63/65}$ ($I = 3/2$) but it is not possible to simulate the superhyperfine with the nitrogen atoms. The simulation gives $g_{\text{iso}} = 2.110$, ($\text{Cu}^{63/65}$) $A_{\text{iso}} = 72.0$ Gauss.

Fluid solution spectrum of Cu(1)(OTf)_2 at X-band (9.42 GHz) in iPrOH/dcm and at 290 K

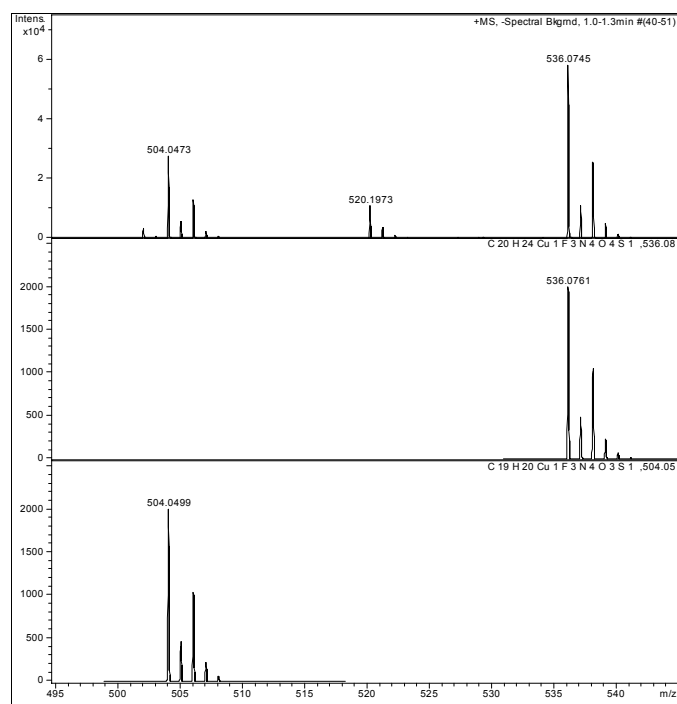


The simulation of the frozen solution spectrum at X-band and 100 K gives an axial set of g values and A values with $g_{\perp} = 2.054$, $g_{\parallel} = 2.218$ and $A_{\perp} = 15.0$ Gauss, $A_{\parallel} = 184.0$ Gauss.

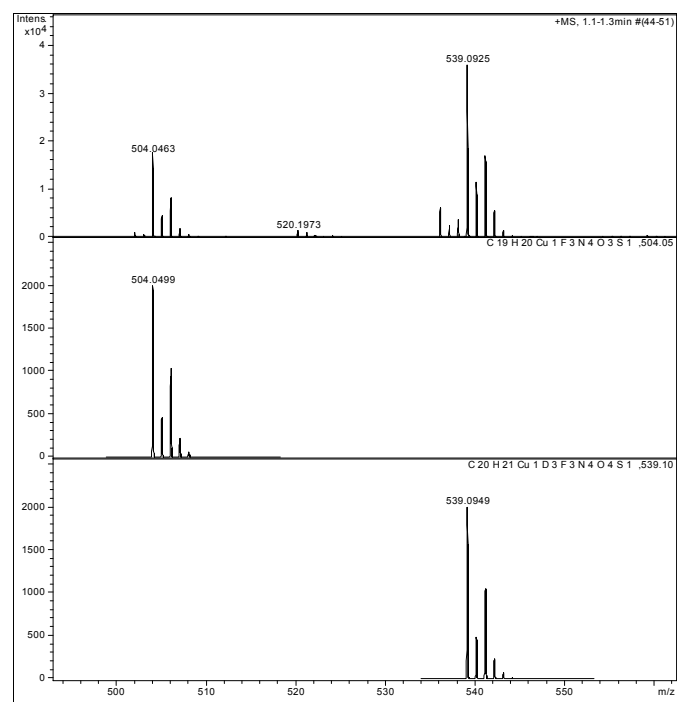
Frozen solution spectrum of Cu(1)(OTf)_2 at X-band (9.42 GHz) in iPrOH/dcm and at 100 K



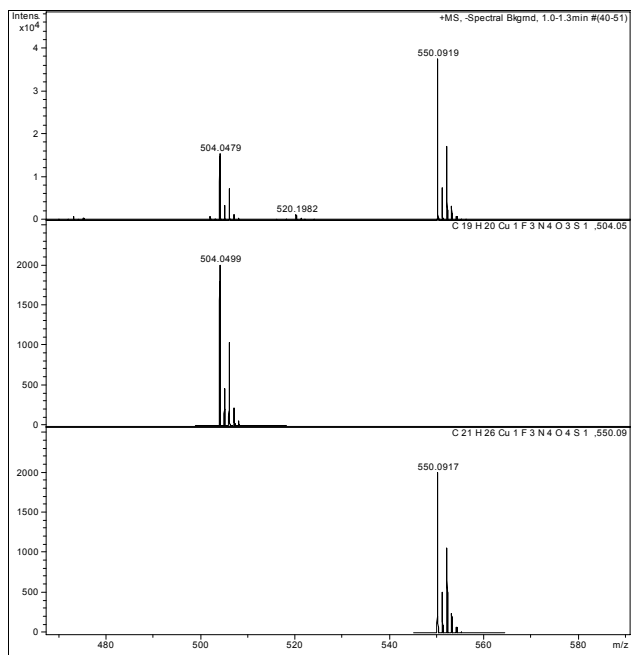
MS Analysis:



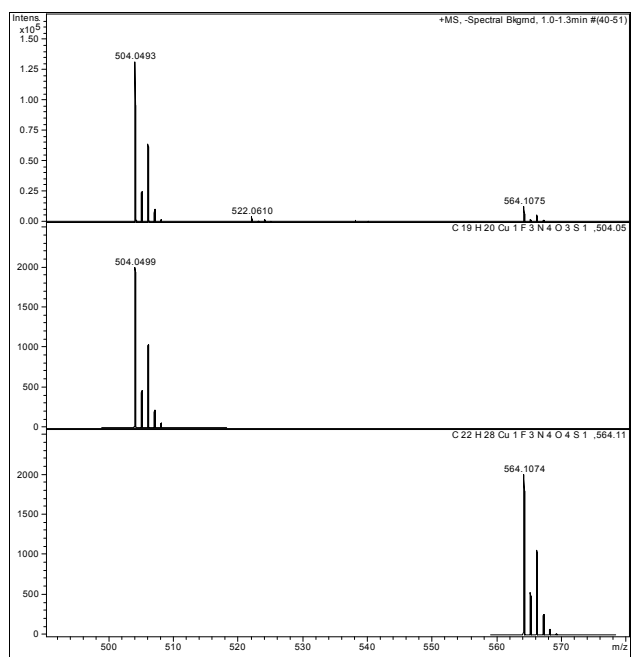
MS of Cu(1-MeOH)(OTf)⁺ in MeOH



MS of Cu(1-MeOH)(OTf)⁺ in CD₃OD



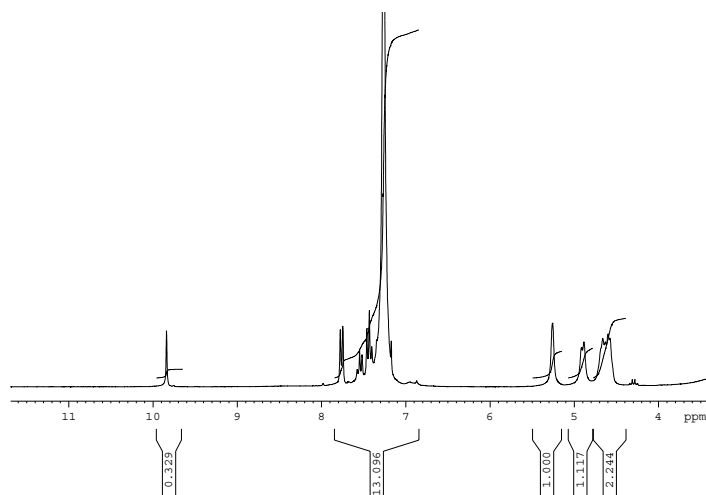
MS of Cu(1-EtOH)(OTf)^+ in EtOH



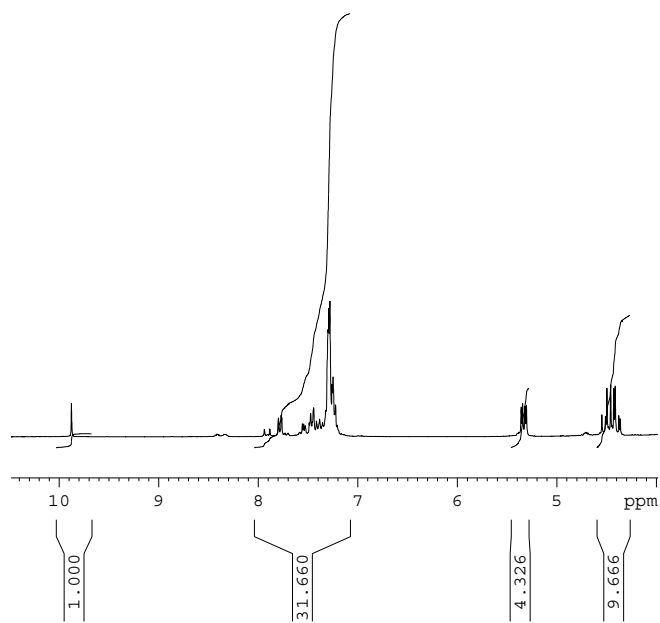
MS of Cu(1)(OTf)^+ in IPA

Catalytic data: (Typical NMR spectra)

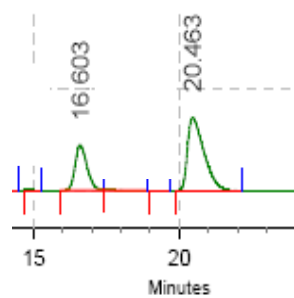
Nitroethane + benzaldehyde Cu(9)(OTf)₂



Nitromethane + benzaldehyde Cu(6)(OTf)₂

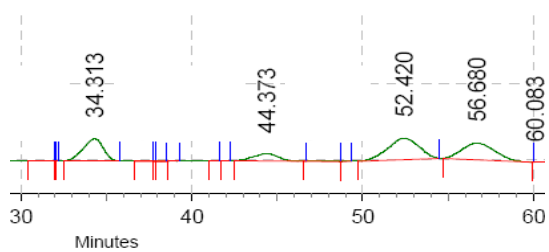


Selected Chromatography results Benzaldehyde + nitromethane Cu(9)(OTf)₂



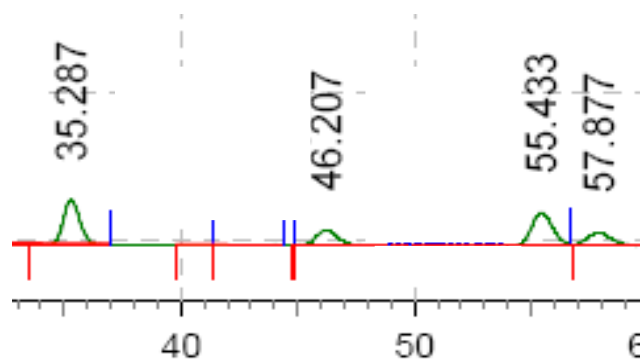
16.603 106546337
20.463 234058080

Benzaldehyde + nitroethane Cu(9)(OTf)₂



34.313 39564704
44.373 16225541
52.420 59732284
56.680 48373393

Benzaldehyde + nitroethane achiral catalyst



35.287	12067962
46.207	5409077
55.433	11660073
57.877	5386671