# Structural origins of a dramatic variation in catalyst efficiency in enantioselective alkene aziridination; implications for design of ligands based on planar chiral biaryldiamines

SUPPORTING INFORMATION

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## General experimental details

Catalytic reactions procedures were carried out under an inert atmosphere of argon by using a dual manifold vacuum/argon line and standard schlenk techniques, or in an MBraun glove box. All solvents were dried by refluxing for three days under dinitrogen over the appropriate drying agents (sodium for toluene; potassium for THF; sodium-potassium alloy for diethyl ether, petroleum ether and pentane; calcium hydride for dichloromethane) and degassed before use. Storage of solvents was in glass ampoules under argon. All glassware, cannulae and Celite were stored in an oven (>100°C) and flame dried immediately prior to use. Deuterated solvents were freeze-thaw-degassed and dried by refluxing over potassium (or calcium hydride for $CD_2Cl_2$) before being vacuum transferred to a clean, dry Young's tap ampoule and being stored in the glove box. Deuterated chloroform was dried over molecular sieves (4A).

NMR spectra were recorded on Bruker ACF-250, DPX-300, DPX-400 and ACP-400 spectrometers and the spectra referenced internally using residual protio solvent resonances

relative to tetramethylsilane (δ = 0 ppm). Mass spectra were obtained using VG Autospec and Micromass Autospec mass spectrometers. Infra red spectra were obtained either as Nujol mulls or by evaporation of dichloromethane solutions onto IR plates, using Perkin-Elmer FTIR spectrometer. Elemental analyses were performed by Warwick Analytical Services on a Leeman Labs CE-440 analyser. HPLC experiments were performed using a Kontron instrument; detector 332, system 320. Column chromatography was performed using a selection of column widths and 60 μm flash silica. Thin layer chromatography was performed using Polygram 0.25 mm silica layer foil backed plates.

**Synthesis of (±)-$L^2$ – [*N*,*N*′-bis-(4-*tert*-butyl-benzylidene)-6,6′-dimethylbiphenyl-2,2′-diamine]**

(±)-2,2′-Diamino-6,6′-dimethylbiphenyl (0.5 g, 2.36 mmol) and 4-*tert*-butylbenzaldehyde (0.76 g, 4.72 mmol) were dissolved in methanol (10 ml) stirred at R.T. for 10 min. to produce a white crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration, washed with cold methanol and dried *in vacuo*. Yield = 0.76 g, 65%. m.p. = 165°C.

$^1$H NMR ($CDCl_3$): δ 8.18 (s, 2H, N=CH), 7.48 (d, 4H, J=9.9 Hz, Ar-H), 7.35 (d, 4H, J=9.9 Hz, Ar-H), 7.21 (t, 2H, J=9.3 Hz, Ar-H), 7.07 (d, 2H, J=8.7 Hz, Ar-H), 6.79 (d, 2H, J=8.7 Hz, Ar-H), 2.05 (s, 6H, Me), 1.31 (s, 18H, $^t$Bu).

$^{13}$C{$^1$H} NMR ($CDCl_3$): δ 159.55 (N=CH), 154.55, 151.67, 137.31, 134.43, 132.38, 128.68, 128.02, 126.86, 125.82, 116.04 (Ar), 31.59 ($^t$Bu), 20.42 (Me).

EA for $C_{36}H_{40}N_2$, Calculated % C, 86.35; H, 8.05; N, 5.60. Found % C, 86.44; H, 8.05; N, 5.57.

IR ($CH_2Cl_2$) ν $cm^{-1}$: 3056, 2961 (s), 2865, 1630 (s), 1607, 1566, 1456, 1364, 1308, 1267, 1216, 1180, 1105, 1016, 941, 830, 784, 746, 552.

MS (EI$^+$): m/z 500 ($M^+$), 485 ($M^+$- Me).

MS ($CI^+$) m/z 501 ($M^+$).

**Synthesis of (+)-$L^2$.**

(+)-2,2′-Diamino-6,6′-dimethylbiphenyl (0.5 g, 2.36 mmol) and 4-*tert*-butylbenzaldehyde (0.76 g, 4.72 mmol) were dissolved in methanol (10 ml) stirred at reflux for 2 h to produce a red viscous oil. The supernatant was decanted and the red oil was dried *in vacuo*. Yield = 1.1 g, 90%.

**Synthesis of (±)-$L^3$ - [*N*,*N*′-bis-(2-naphthylidene)-6,6'-dimethylbiphenyl-2,2'-diamine].**

(±)-2,2′-Diamino-6,6′-dimethylbiphenyl (1.1 g, 5.1 mmol) and 2-naphthylaldehyde (1.6 g, 10.2 mmol) were dissolved in methanol (25 ml) stirred under reflux for 5 h to produce a bright yellow crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration. The solid was redissolved in a hot 4:1 methanol:dichloromethane solution, filtered and concentrated until the onset of crystallisation. The solution was cooled to -30°C, the solid was isolated by filtration, washed with hexane and dried *in vacuo*. Yield = 2.1 g, 85%. m.p. = 168°C.

$^1$H NMR ($CDCl_3$): δ 8.25 (s, 2.0H, N=CH), 7.83–7.80 (m, 10H, Ar-H), 7.75-7.45 (m, 4.0H, Ar-H), 7.28-7.23 (t, 3.0H, Ar-H), 7.12 (d, J=7.5Hz, 1.9H, Ar-H), 6.84 (d, 2.0H, J=7.5Hz, Ar-H), 2.12 (s, 6.0H, Me).

$^{13}$C{$^1$H} NMR ($CDCl_3$): δ 159.56 (N=C), 151.40, 136.94, 134.76, 134.24, 132.91, 132.05, 130.83, 128.62, 128.33, 127.82, 127.22, 126.75, 126.36, 123.78, 115.50 (Ar), 20.00 (Me).

$^1$H NMR ($CD_2Cl_2$ ): δ 8.37 (s, 2.0H, N=CH), 7.90–7.77 (m, 10.0H, Ar-H), 7.60-7.51 (m, 4.0H, Ar-H), 7.32 (t, J=7.7Hz, 1.9H, Ar-H), 7.18 (d, J=7.3Hz, 1.8H, Ar-H), 6.91 (d, J=7.7Hz, 2.0H, Ar-H), 2.13 (s, 6.0H, Me).

EA for $C_{36}H_{28}N_2$, Calculated % C, 88.49; H, 5.77; N, 5.73. Found % C, 87.85; H, 5.72; N, 5.72.

MS ($EI^+$): m/z 488 ($M^+$), 473 ($M^+$- $CH_3$).

IR ($CD_2Cl_2$) ν $cm^{-1}$: 3440 (b), 3054, 2917, 2859, 1925, 1620 (s), 1571 (s), 1453, 1334, 1264, 1239, 1175, 1120, 1017, 969, 943, 895, 858, 819, 764, 745 (s), 474.

**Synthesis of (+)-$L^3$**

(+)-2,2′-Diamino-6,6′-dimethylbiphenyl (1.1 g, 5.1 mmol) and 2-naphthylaldehyde (1.6 g, 10.2 mmol) were dissolved in methanol (25 ml) stirred under reflux for 5 h. The reaction mixture was allowed to cool to RT where an orange oil precipitated from the solution. On cooling to -30°C a yellow solid formed from the orange oil, which was isolated by filtration and washed with cold methanol. Yield = 1.8 g, 80%.

HPLC [Chiracel OD, hexane:IPA 90:10, 0.5 ml/min]: Rt = 9.8 (0.4%), 11.5 (99.6%) min. E.E. = 99.2%.

**Synthesis of (±)-$L^4$ – [*N*,*N*′-bis-(2,6-dichlorobenzylidene)-6,6′-dimethylbiphenyl-2,2′-diamine].**

(±)-2,2′-Diamino-6,6′dimethylbiphenyl (1.0 g, 4.7 mmol) and 2,6-dichlorobenzaldehyde (1.65 g, 9.4 mmol) were dissolved in methanol (25 ml) stirred under reflux for 3 h to produce a bright yellow crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration, washed with cold methanol and recrystallised from ethanol. Yield = 2.2 g, 89%. m.p. = 166°C.

$^1H$ NMR ($CDCl_3$): δ 8.50 (s, 2.0H, N=CH), 7.29-6.84 (Ar-H, 13.0H), 2.05 (s, 6.0H, Ar- Me).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.68 (N=C), 150.96, 137.08, 134.95, 132.41, 131.82, 130.06, 128.46, 127.31, 115.70 (Ar), 19.84 (Me).

MS ($EI^+$): m/z 527 ($M^+$), 511 ($M^+$-$CH_3$), 353 ($M^+$-$NC_7H_4Cl_2$).

EA for $C_{28}H_{20}N_2Cl_4$, Calculated % C, 63.90; H, 3.83; N, 5.32. Found % C, 63.89; H, 3.80; N, 5.36.

IR ($CD_2Cl_2$) ν $cm^{-1}$: 3441 (b), 3056, 2915, 2358, 1635, 1575, 1557, 1455, 1430 (s), 1375, 1265, 1210, 1186, 1094, 939, 775 (s), 749 (s).

**Synthesis of (+)-$L^4$.**

(+)-2,2′-Diamine-6,6′dimethylbiphenyl (1.0 g, 4.7 mmol) and two equivalents of 2,6-dichlorobenzaldehyde (1.65 g, 9.4 mmol) were dissolved in methanol (25 ml) stirred under reflux for 15 h with a Soxhlet apparatus attached filled with sodium sulphate. On cooling a brown viscous liquid precipitated from the solution. The supernatant was decanted and the oil was dried under vacuum, the viscous oil gradually solidified. 10% of the mono substituted diamine was present in the mixture. The chiral non-racemic (+)-$L^4$ was isolated pure by freeze drying the gummy solid to remove any methanol present, then dissolving in diethyl ether and adding 4:1 hexane:ethyl acetate until precipitation began, then cooling to -30°C, the yellow crystalline solid was isolated by filtration and dried. Yield = 1.4 g, 56%.

A crystal suitable for X-ray structural determination was chosen and the molecular structure solved. Refinement of the Flack parameter showed that the correct absolute structure was the *R*-isomer.

**Synthesis of (±)-$L^5$ – [*N*,*N*′-bis(2,4,6-trimethylbenzylidene)- 6,6′-dimethylbiphenyl-2,2′-diamine]**

(±)-2,2′-Diamino-6,6′dimethylbiphenyl (2.5 g, 11.8 mmol) and two equivalents of 2,4,6-trimethylbenzaldehyde (3.5 g, 23.5 mmol) were dissolved in methanol (25 ml) stirred under reflux for 1 h to produce a light yellow crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration, washed with cold methanol and dried under reduced pressure. The compound was recrystallised from hot diethyl ether. Yield = 4.9 g, 87%. m.p. = 138°C.

$^1$H NMR ($CDCl_3$): δ 8.55 (s, 2.1H, N=CH), 7.22 (t, $^3J_{HH}$ = 7.6Hz, 2.0H, Ar-H), 7.06 (d, $^3J_{HH}$

= 7.6Hz, 2.1H, Ar-H), 6.75 (d, $^3J_{HH}$ = 7.6Hz, 2.1H, Ar-H), 6.75 (s, 4.1H, Mes-H), 2.22 (s, 6.0H, Ar- Me), 2.09 (s, 12.0H, Mes), 2.03 (s, 6.1H, Mes).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.30 (C=N), 152.27, 139.19, 138.65, 136.69, 132.41, 130.14, 129.45, 127.71, 126.37, 115.38 (Ar), 20.98 ($CH_3$), 20.50, 19.85 (Mes-$CH_3$).

MS ($EI^+$): m/z 472 ($M^+$), 457 ($M^+$-$CH_3$).

EA for $C_{34}H_{36}N_2$, Calculated % C, 86.40; H, 7.68; N, 5.93. Found % C, 86.47; H, 7.70; N, 5.91.

IR ($CD_2Cl_2$) ν $cm^{-1}$: 3057 (s), 2917 (s), 2860 (s), 2731, 2358, 1925, 1631 (s), 1607 (s), 1573 (s), 1453 (s), 1377, 1264, 1207, 1153, 1031, 973, 950, 888, 845 (s), 778 (s), 759, 743 (s), 704, 557.

**Synthesis of (+)-$L^5$**

As racemic $L^5$, except that the reaction mixture was refluxed for 5h before isolation of the chiral non-racemic ligand from a cooled methanolic solution (-30°C). Yield = 52%.

**Synthesis of (+)-$L^6$ – [*N*,*N*′-bis-(anthracen-9-ylidene)-6,6′-dimethylbiphenyl-2,2′-diamine].**

(+)-2,2′-Diamino-6,6′-dimethylbiphenyl (1.0 g, 4.7 mmol) and anthracene-9-carbaldehyde (93% 2.1 g, 10.1 mmol) were dissolved in methanol (15 ml) stirred at reflux for 5 h to produce a bright yellow crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration, washed with cold methanol and dried *in vacuo*. From $^1H$ NMR analysis it was found that approximately 20% of the isolated solid was unreacted biphenyldiamine and aldehyde. The solid was redissolved in 15:1 hexane:ethyl acetate and filtered through a small plug of silica to remove the biphenyldiamine, the resultant mixture was evaporated to dryness the aldehyde was sublimed from the mixture (2 x $10^{-6}$ atm. 130-140°C) the residue was extracted into dichloromethane and dried *in vacuo* to give a

bright yellow powder. Yield = 2.56 g, 93%.

$^1$H NMR ($CD_2Cl_2$): δ 9.58 (s, 2.2H, N=CH), 8.43 (s, 1.9H, Ph), 8.31 (d, 4.0H, Ph), 7.96 (d, 4.0H, Ph), 7.65 (t, 2.0H, Ph), 7.44 (m, 5.8H, Ph), 7.31 (m, 5.9H, Ph), 2.33 (s, 6.0H, Me).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ 160.28 (N=CH), 153.43, 138.10, 133.69, 131.93, 131.09, 131.02, 129.54, 129.44, 128.32, 127.97, 127.69, 125.97, 125.51, 117.09 (Ar), 20.70 (Me).

MS ($EI^+$) m/z: 588 ($M^+$).

MS ($CI^+$) m/z: 607 ($MNH_4^+$), 589 ($MH^+$).

EA for $C_{44}H_{32}N_2$, Calculated % C, 89.76; H, 5.48; N, 4.76. Found % C, 89.33; H, 5.34; N,3.84.

IR ($CH_2Cl_2$) ν cm$^{-1}$: 3051, 2918, 2862, 236., 1920, 1671, 1626, 1572, 1520, 1451, 1377, 1310, 1263, 1239, 1176, 1158, 1103, 1066, 1048, 1021, 973, 950, 890, 840, 784, 757, 732 (s), 610.

**Synthesis of (±)-L$^7$ - [*N,N'*-bis-(4-nitrobenzylidene)-6,6'-dimethylbiphenyl-2,2'-diamine].**

(±)-2,2'-Diamino-6,6'-dimethylbiphenyl (1.0 g, 4.7 mmol) and p-nitrobenzaldehyde (1.41 g, 9.4 mmol) were dissolved in methanol (25 ml) stirred under reflux for 2 h to produce a bright yellow crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration, washed with cold methanol and dried *in vacuo*. Yield = 2.0 g, 88%. m.p. = 278°C.

$^1$H NMR ($CDCl_3$): δ 8.28 (s, 2.0H, N=CH), 8.17 (d, $^3J_{HH}$ = 8.9 Hz, 4.0H, Ar-H), 7.62 (d, $^3J_{HH}$ = 8.7Hz, 4.0H, Ar-H), 7.28 (t, $^3J_{HH}$ = 7.7 Hz, 2.0H, Ar-H), 7.16 (d, $^3J_{HH}$ = 7.5 Hz, 2.0H, Ar-H), 6.88 (d, $^3J_{HH}$ = 7.7 Hz, 2.0H, Ar-H), 2.04 (s, 6.0H, Me).

MS ($EI^+$): m/z 478 ($M^+$).

EA for $C_{28}H_{22}N_4O_4$, Calculated % C, 70.28; H, 4.63; N, 11.71. Found % C, 70.19; H, 4.66; N, 11.63.

IR ($CD_2Cl_2$) ν cm$^{-1}$: 3473 (b), 2359, 1638, 1600, 1523, 1450, 1343 (s), 1204, 1106, 1109, 981, 939, 855, 841, 784, 744, 689, 586, 471.

**Synthesis of $[\{Cu(I)(L^2)\}_2][OTf]_2$ (1)**

$L^2$ and half an equivalent of $(CuOTf)_2.C_6H_6$ were dissolved in $d_2$-dichloromethane. Concentration of the solution resulted in formation of crystals suitable for X-ray diffraction.

$^1H$ NMR ($CD_2Cl_2$): δ8.62 (s, 2.0H, N=CHAr), 7.42 (d, 2.0H, Ar-H), 7.26 (s, $C_6H_6$), 7.19 (t, $^3J_{HH}$ = 7.5Hz, Ar-H), 7.15 (d, $^3J_{HH}$ = 7.5Hz, Ar-H), 7.00(d, $^3J_{HH}$ = 8.3Hz, 6H, Ar-H), 1.73(s, 6.0H, $CH_3$), 1.12(s, 18H, $^t$Bu).

$^{13}C$ NMR {H} ($CD_2Cl_2$): δ172.99 (N=C), 160.71, 149.62, 140.25, 133.13, 131.99, 130.81, 129.86, 129.73, 126.76, 121.99 (Ar), 129.07 ($C_6H_6$), 31.35 ($^t$Bu), 20.35 (Me).

MS ($EI^+$) m/z: 712 $[\{Cu(I)L^2\}][OTf]^+$, 500 $[L^{2+}]$, 485 $[L^2 - CH_3^+]$.

MS ($CI^+$) m/z: 713 $[Cu(I)(L^2)H][OTf]^+$, 649 $[(M^+) - Cu]$, 563 $[Cu(I)(L^2)]^+$, 501 $[L^2H^+]$, 485 $[L^2 - CH_3^+]$, 340 $[L^2 - N{=}CHC_6H_4C(CH_3)_3^+]$.

MS ($FAB^+$) m/z: 1277 ($[\{CuL^2\}_2][OTf]^+$), 1128 $[\{CuL^2\}_2^+]$, 1063 $[Cu(L^2)_2^+]$, 775, 563 $[Cu(L^2)^+]$.

High Resolution MS (EI+) Calculated Mass ($M^+$) 712.200774. Found 712.193039.

**Synthesis of $[\{Cu(I)(L^3)\}_2][OTf]_2$ (2)**

$L^3$ and half an equivalent of $(CuOTf)_2.C_6H_6$ were dissolved in $d_2$-dichloromethane. Concentration of the solution resulted in the formation of crystals suitable for X-ray diffraction.

$^1H$ NMR ($CD_2Cl_2$): δ8.77 (s, 2.0H, N=CHAr), 7.74 (s, 1.9H, Ar-H), 7.38 – 7.14 (m, Ar-H), 7.26 (s, $C_6H_6$), (aromatics 15H), 7.06 (d, $^3J_{HH}$ = 7.9Hz, 2.0H, Ar-H), 6.84 (d, $^3J_{HH}$ = 8.7Hz, 1.9H, Ar-H), 6.64 (d, $^3J_{HH}$ = 8.6Hz, 1.9H, Ar-H), 1.96 (s, 6.0H, $CH_3$).

$^{13}C$ NMR {H} ($CD_2Cl_2$): δ174.03 (N=C), 164.90, 149.90, 140.46, 136.34, 133.05, 132.58, 132.38, 130.46, 129.57, 129.42, 129.19, 129.09, 128.41, 128.09, 122.25, 121.66 (Ar), 20.73 (Me).

MS (FAB$^+$) m/z 1253 ([{CuL$^3$}$_2$][OTf]$^+$), 1104 ([{CuL$^3$}$_2$]$^+$), 1040 ([Cu{L$^3$}$_2$]$^+$), 552 ([CuL$^3$]$^+$).

**Synthesis of [Cu(L$^4$)(CH$_3$CN)$_2$][BF$_4$].CH$_2$Cl$_2$ (3).CH$_2$Cl$_2$**

A Schlenk was charged with [Cu(CH$_3$CN)$_4$][BF$_4$] (72.4 mg, 230 μmol) and L$^4$ (133 mg, 253 μmol), evacuated and flushed with argon. The two solids were dissolved in dichloromethane with stirring and an equal volume of pentane was added to the yellow solution. Upon cooling the solution yellow needle like crystals formed.

The crystals were of sufficient quality for X-ray analysis.

EA Theoretical: C 46.98%; H 3.35%; N 6.64%. Found: C 47.44%, H 3.37%, N 6.35%.

$^1$H NMR (CD$_2$Cl$_2$): δ 8.54 (s, 2.0H, N=CH), 7.44-7.00 (m, 12H, Ar-H), 2.05 (s, 6.0H, Me), 1.95 (s, 6.0H, CH$_3$CN).

$^{13}$C {$^1$H} NMR (CD$_2$Cl$_2$): δ 162.59 (N=CH), 139.68, 134.98, 133.02, 132.06, 130.04, 129.96, 129.50, 118.22 (Ar), 20.23 (Me), 2.53 (CH$_3$CN).

**Synthesis of [Cu(L$^4$)][OTf] [triflate analogue of (3)]**

The L$^4$ and half an equivalent of (CuOTf)$_2$.C$_6$H$_6$ were dissolved in d$_2$-dichloromethane.

$^1$H NMR (CD$_2$Cl$_2$): δ8.46 (s, 2H, N=CHAr), 7.30 (t, $^3J_{HH}$ = 7.6Hz, Ar-H), 7.26 (s, C$_6$H$_6$), 7.20 (bs, Ar-H), 7.30- 720 (aromatics 15H), 1.89 (s, 6.0H, CH$_3$).

$^{13}$C NMR {H} (CD$_2$Cl$_2$): δ162.56 (N=C), 135.10, 132.97, 131.25, 130.08, 129.75, 129.07, 118.75 (Ar), 20.31 (Me).

MS (EI) m/z 738 {[Cu(L$^4$)][OTf]$^+$}, 589 {[Cu(L$^4$)]$^+$}, 527 [L$^{4+}$].

MS (CI) m/z 589{[Cu(L$^4$)]$^+$}, 527 [L$^{4+}$].

IR (CD$_2$Cl$_2$) ν cm$^{-1}$: 3339, 3121, 2302, 2196, 1750, 1628, 1579, 1560, 1433, 1385, 1313, 1270, 1234, 1211, 1170.

**Synthesis of $[CuL^5(CH_3CN)_2][BF_4]$ (4)**

$L^5$ (1.1 equiv.) and $[Cu(CH_3CN)_4][BF_4]$ (1 equiv.) were dissolved in dichloromethane (25 ml) with warming. The yellow solution was stirred for 30 minutes, concentrated and filtered. The filtrate was placed in the freezer (-30°C); the yellow crystals obtained were suitable for X-ray structural determination.

$^1H$ NMR ($CDCl_3$): δ8.55 (s, 2.1H, N=CH), 7.39 (t, $^3J_{HH}$ = 7.6Hz, 2.0H, Ar-H), 7.25 (d, $^3J_{HH}$ = 7.6Hz, 1.9H, Ar-H), 6.94 (d, $^3J_{HH}$ = 7.6Hz, 1.9H, Ar-H), 6.81 (s, 4.0H, Mes-H), 2.23 (s, 6.0H, Ar-$CH_3$), 2.02 (s, 6.1H, Mes), 1.94 (s, 12.1H, Mes), 1.86 (s, 6.2H, $CH_3CN$).

EA for $C_{38}H_{42}N_4$, Calculated % C, 64.37; H, 6.00; N, 7.95. Found % C, 64.30; H, 5.95; N, 7.81.

MS (CI) m/z 617{M-$BF_4$}.

IR ($CH_2Cl_2$) ν 2360 (s), 1573 (m), 1057 (s).

**Synthesis of $[Cu(L^5)][OTf]$ [triflate analogue of (4)]**

The $L^5$ and half an equivalent of $(CuOTf)_2.C_6H_6$ were dissolved in $d_2$-dichloromethane.

$^1H$ NMR ($CD_2Cl_2$): δ8.54 (s, 2.0H, N=CHAr), 7.30 (t, $^3J_{HH}$ = 7.7Hz, 1.9H, Ar-H), 7.22 (s, 2.9H, $C_6H_6$), 7.18 (d, $^3J_{HH}$ = 7.5Hz, 1.8H, Ar-H), 6.93 (d, $^3J_{HH}$ = 7.7Hz, 2.0H, Ar-H), 6.73 (s, 4.1H, Ar-H), 2.14 (s, 6.3H, Mesityl-$CH_3$), 1.94 (s, 12H, Mesityl-$CH_3$), 1.91 (s, 6H, $CH_3$).

$^{13}C$ NMR {H} ($CD_2Cl_2$): δ169.42 (N=C), 149.24, 141.48, 139.11, 137.52, 130.98, 130.77, 130.26, 129.98, 128.93, 119.18 (Ar), 129.82 ($C_6H_6$), 21.73 (mesityl), 20.28 (mesityl), 20.21 ($CH_3$).

MS ($FAB^+$) m/z: 684 ($[CuL^5][OTf]^+$), 535 ($[CuL^5]^+$), 471 ($L^{5+}$).

**Chromene=NTs - [*N*-*p*-Toluenesulphonyl-2,3-(6-Acetyl-2,2-dimethyl-chroman-3,4-yl)aziridine] (6)**

$R_f$ = 0.25 in 2:1 hexane:ethyl acetate.

$^{1}$H NMR ($CDCl_3$): δ 7.93 (s, 1H, Ar-H), 7.85-7.82 (d,d, 1H, *J* = 8.4 Hz, 2H, *J* = 8.1 Hz, Ar-H), 7.33 (d, 2H, *J* = 8.1 Hz, Ar-H), 6.81 (d, 1H, *J* = 8.4 Hz, Ar-H), 3.97 (d, 1H, *J* = 7.3 Hz, C*H*-aziridine), 3.37 (d, 1H, *J* = 7.3 Hz, C*H*-aziridine), 2.54 (s, 3H, $CH_3CO$), 2.43 (s, 3H, Ar-$CH_3$), 1.31 (s, 3H, $CH_3$), 1.25 (s, 3H, $CH_3$).

$^{13}$C NMR {H} ($CDCl_3$): δ 194.22 (*C*OMe), 154.77, 142.89, 132.68, 128.94, 128.84, 127.95, 127.74, 125.96, 116.26, 115.90 (Ph), 70.86 ($C(Me)_2$), 47.62 ($CH_{aziridine}$), 37.56 ($CH_{aziridine}$), 24.26, 23.82, 21.72, 19.61 (Me).

M.P (DSC) 160°C

MS (EI+) m/z : 372 ($M+H^+$), 216 ($M^+$- $SO_2C_6H_4CH_3$), 91 ($C_6H_4CH_3^+$), 43 ($CH_3CO^+$).

IR (Nujol): 1669.3 ν (C=O), 1456.4 δas ($CH_3$), 1377.0, 1365.5 δs ($CH_3$), 1328.5 νas ($SO_2$), 1267.3 ν (C-O-C), 1160.7 νs ($SO_2$), 904.0, 868.3 γ (CH) 1H, 830.2, 825.5 γ (CH) 2H.

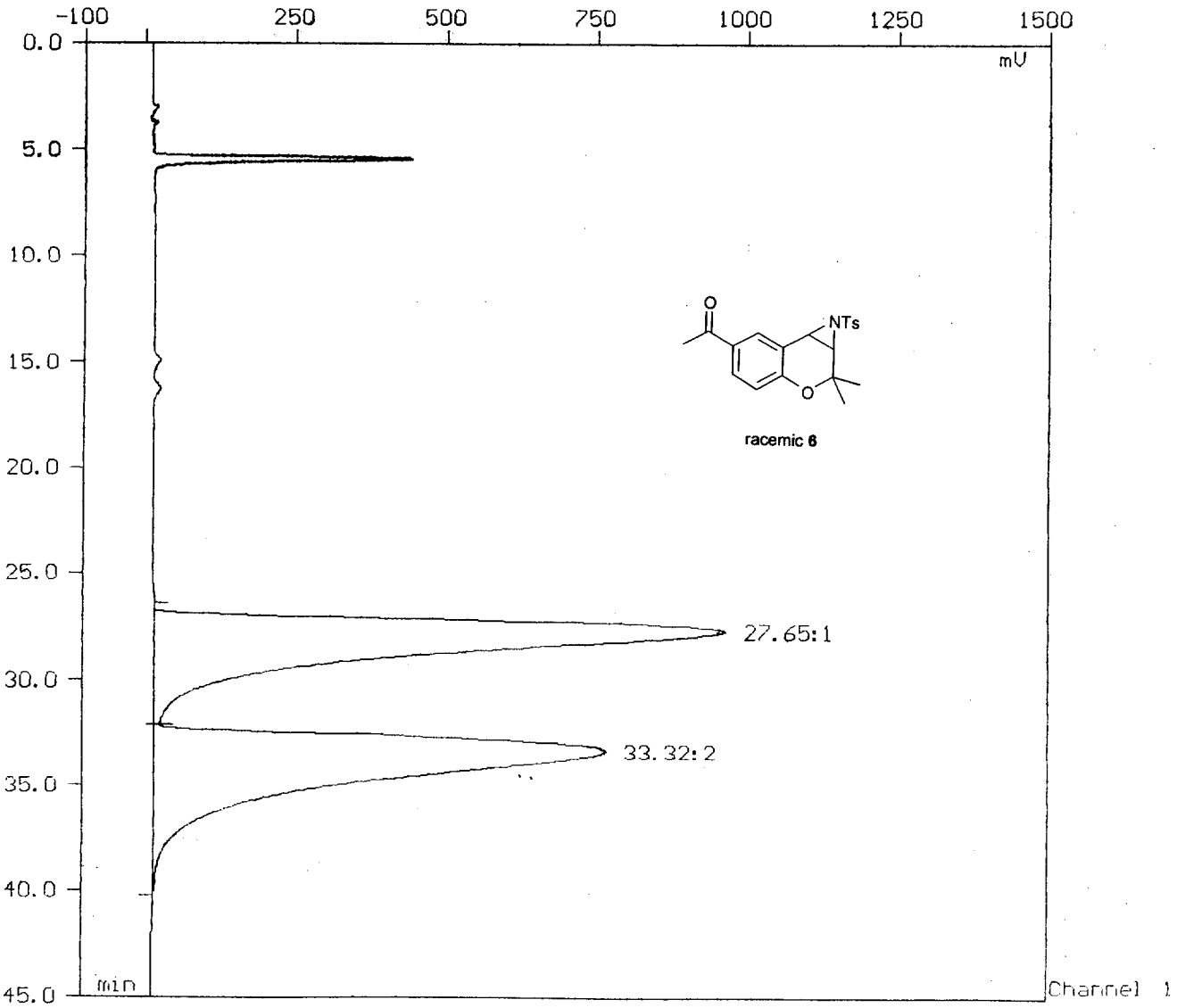
High Resolution MS (EI+) Calculated Mass ($M^+$-Ts) 216.102454. Found 216.101996.

Chiral HPLC analysis [Chiralcel OD hexane : IPA (95:5), 1 ml/min]: $R_t$ of enantiomers 27.7, 33.3 min. Sample traces follow below.

CONTRON DATA SYSTEM 450-MT2 V3.94 | RESULT REPORT: INTEGRATION

HPLC - KGRAC.SMP (modified): racemic Chromene=NTs
No. 01: kgrac 01.01 Channel 1 Date: 03.12.99 Time: 03:55:42
Program File ..... .....
Method File ..... KG1 ..... bi2np
Peak Table ..... DEFAULT ..... Auto-generated
Parameter Table .. DEFAULT ..... default
Report File ..... DEFAULT ..... Can't open file
Document File .... ..... Can't open file

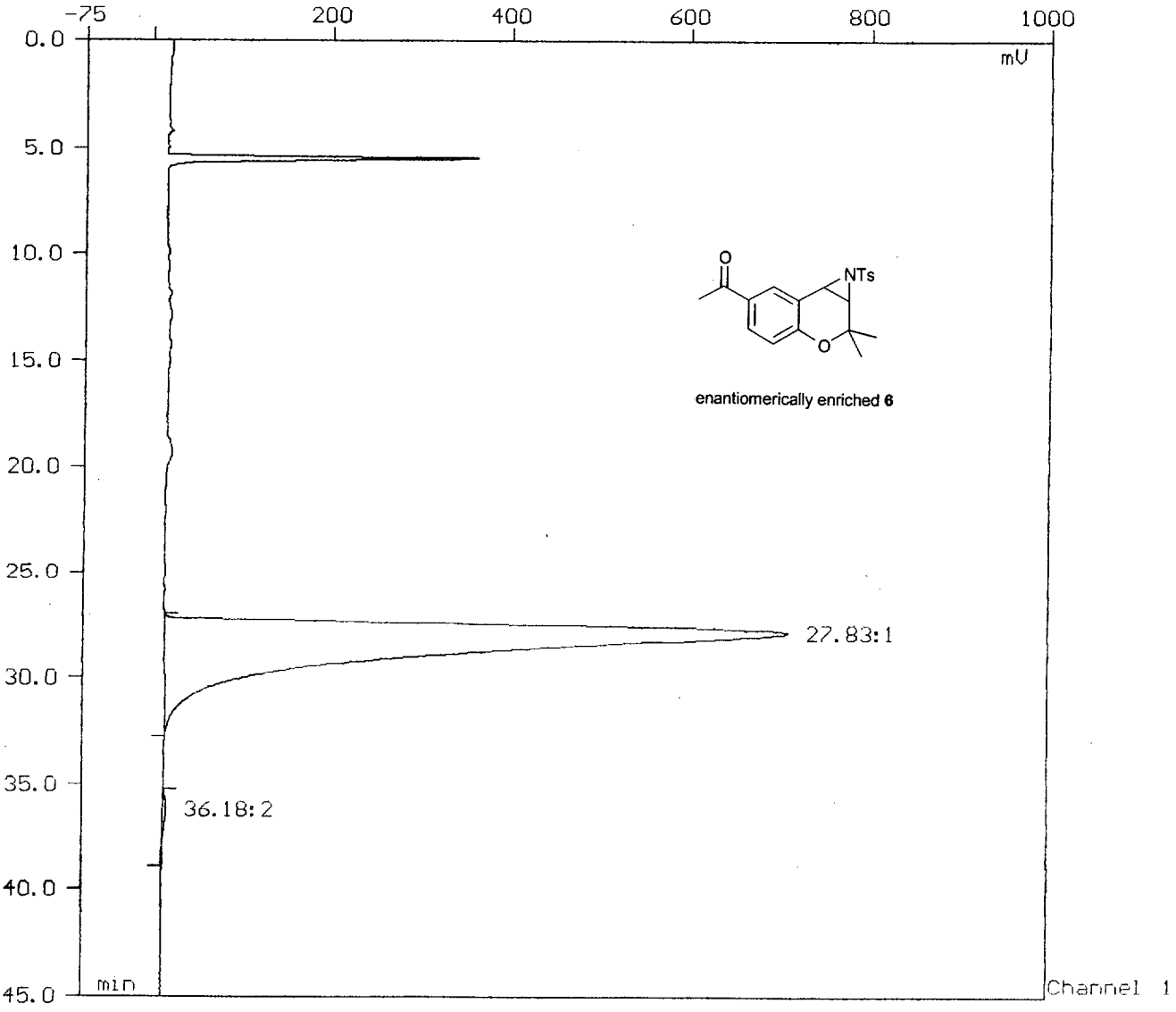
| No. | PNo | Ret.Time min | Type | Substance Name | Area mV*min | Amount | Rel.Area % |
|---|---|---|---|---|---|---|---|
| 1 | ? | 27.65 | ML | ? | 1.7267e+003 | ? | 49.35 |
| 2 | ? | 33.32 | M R | ? | 1.7720e+003 | ? | 50.65 |

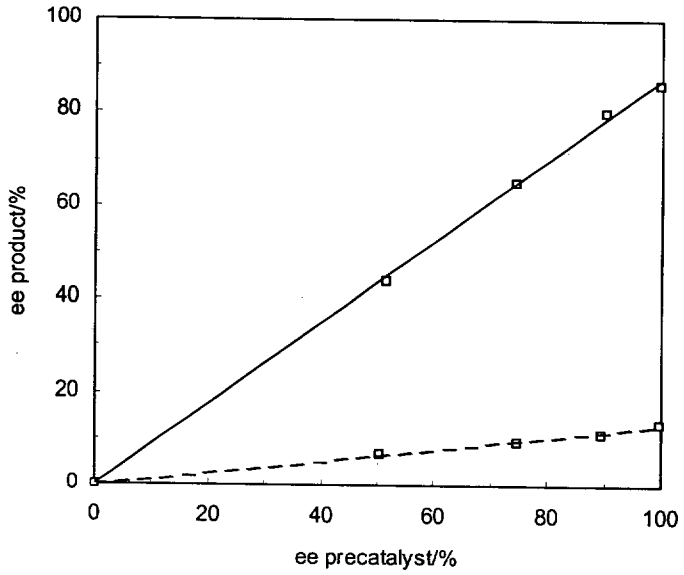


.ONTRON DATA SYSTEM 450-MT2 V3.94 | RESULT REPORT: INTEGRATION

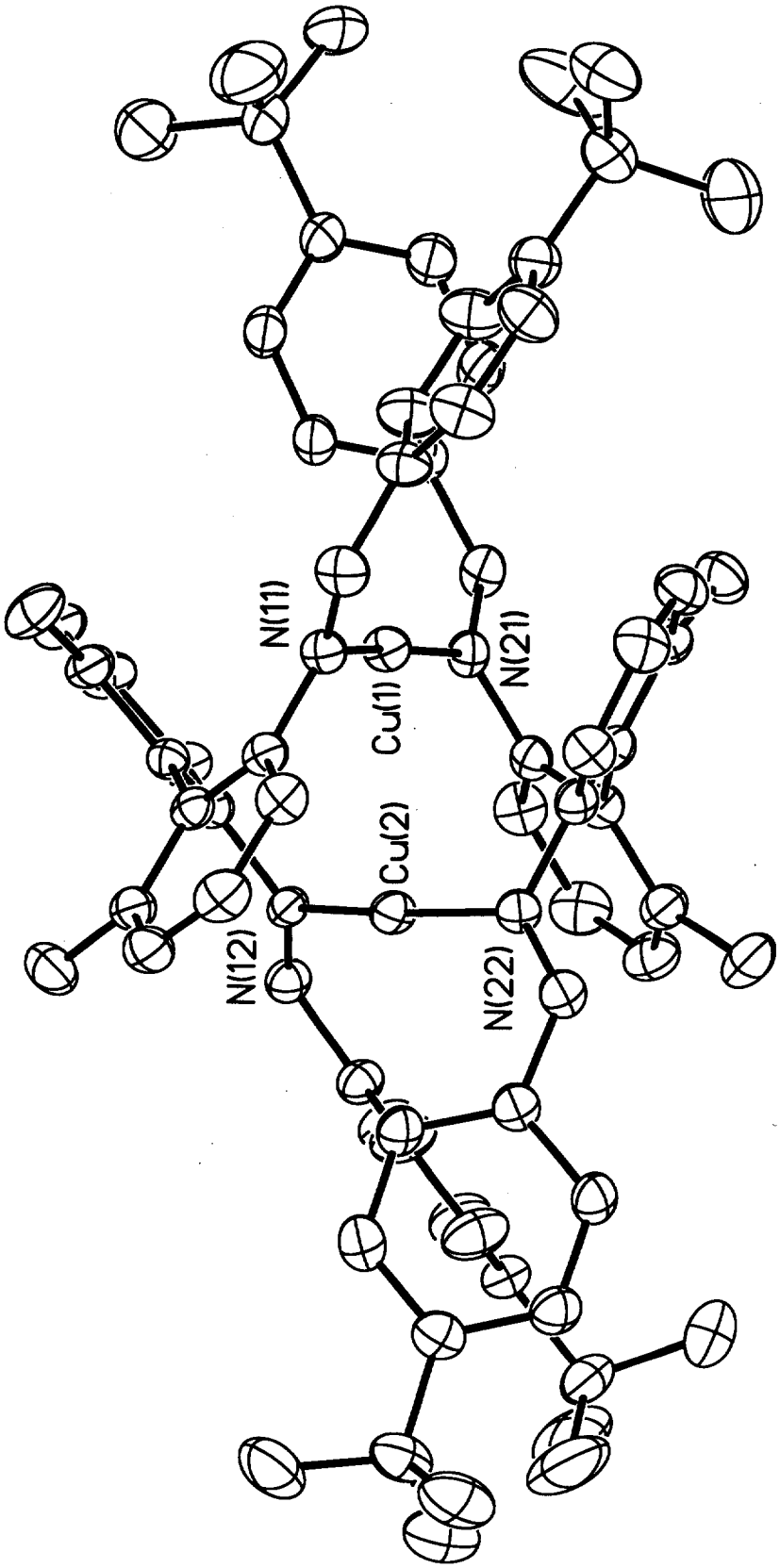
HPLC - KGENT.SMP (modified): Non-Racemic Chromene=NTs
No. 01: kgent 01.01 Channel 1 Date: 03.12.99 Time: 04:49:14
Program File ..... .....
Method File ..... KG1 ..... bi2np
Peak Table ..... DEFAULT ..... Auto-generated
Parameter Table .. DEFAULT ..... default
Report File ..... DEFAULT ..... Can't open file
Document File .... ..... Can't open file

| No. | PNo | Ret.Time min | Type | Substance Name | Area mV*min | Amount | Rel.Area % |
|---|---|---|---|---|---|---|---|
| 1 | ? | 27.83 | MLR | ? | 1.0724e+003 | ? | 99.50 |
| 2 | ? | 36.18 | MLR | ? | 5.4239e+000 | ? | 0.50 |






**Plots of $ee_{ligand}$ *v.* $ee_{product}$ for $L^2$ (dashed line) and $L^4$ (solid line) using $[Cu^I(CH_3CN)_4]BF_4$.** Points are average of at least 2 independent experiments giving a value +/- 2% ee



# CRYSTAL STRUCTURE DETERMINATION

## Structure Solution Log

User: Chris  Data collection Date: 28/7/99

X-ray Mnemonic [6 chars max - unique] Jul199  Directory:

Investigators Sample Code

Collection Temp (deg. C) -93

How was the crystal mounted? (ring) ~~Glue~~/ oil/ ~~tube~~

Crystal size 0.6 x 0.4 x 0.4

Frame time 10's  Frame width

$\delta I/\sigma(I)$ spread

Decay rate (in start of *t._ls) 0.0073 Std Dev. 0.6103 Good.

Batch R-sym (middle of *m._ls) 0.029, 0.026, 0.026, 0.020

Overall R-sym (*m._ls) 0.027

| ~~resolution(d) Sintheta/lamda~~ | to 0.94 | to 0.8 | to 0.74 | |
|---|---|---|---|---|
| %Coverage | 93.60 | 92.01 | 83.76 | Limiting s/l: |
| Redundancy | 1.63 | 1.46 | 1.42 | ~~(0.74)~~ |
| R-sym | 0.026 | 0.027 | 0.027 | (d) at $2\sigma(I)$ |
| Mean sigma | 27.74 | 10.29 | 7.64 | |
| % refls<2sigma (shell) | 17.4 | 28.6 | 82.9 | — |

Cell constants: no of refls to define (in end of *m._ls) (14221) 7111

[Values] A 11.4466 (0.0002)  $\alpha$ 69.387 (0.001)  Vol 3698.71

B 18.1140 (0.0003)  $\beta$ 78.246 (0.00)  (0.15)

C 19.5085 (0.0002)  $\gamma$ 82.443 (0.001)

Absorption/Psi-scan Corrections

| Method | $\mu t$ | R-Int before | R-Int after | Range | Data file name |
|---|---|---|---|---|---|
| FACE(XPREP) | | | | | |
| FACE (ABSPSI) | | | | | |
| PSI-SCAN (SADABS) | | 0.0248 | 0.0156 | | |
| PSI-SCAN (XPREP) | | | | | |

| Sets/subsets of data selected. | | |
|---|---|---|

space group Indications

Str Solution: Method:

Special features of solution and refinement

special modelling

(e.g. disorder); nature of solvent

[NB Print out final .lst]

XRAYDATA.DOC

Experimental data for jul199m

Crystal Data

C75 H82 Cl2 Cu2 F6 N4 O6 S2, M = 1511.55, Triclinic, space group P-1
a = 11.4466(6), b = 18.1140(9), c = 19.5085(6) A ,
alpha = 69.3870(10) deg., beta = 78.2460(10) deg., gamma = 82.4430(10) deg.,
U = 3698.7(3) A^3 (by least squares refinement on 7111 reflection positions),
T =180(2)K, lambda = 0.71073 A, Z = 2,
D(cal) = 1.357 Mg/m^3, F(000) = 1572.
mu(MoK-alpha) = 0.772 mm^-1.
Crystal character: Yellow Block.
Crystal dimensions 0.60 x 0.40 x 0.40 mm,

Data Collection and Processing.

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 180(2)
K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986).
Maximum theta was 28.48 deg.
The hkl ranges were -14/ 15, -21/ 24, -17/ 26.
22072 reflections measured, 16082 unique [R(int) = 0.0165].
Absorption correction by SADABS;
minimum and maximum transmission factors: 0.7373;
0.9280.

no crystal decay

Structure Analysis and Refinement.

Systematic absences indicated
space group P-1
and shown to be correct by successful refinement.

The structure was solved by direct methods
using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by
Fourier methods.

Hydrogen atoms were added at calculated positions and refined using a riding
model with freely rotating methyl groups. Anisotropic displacement
parameters were used for all non-H atoms;
H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for
methyl hydrogen atoms) times the equivalent isotropic displacement parameter
of the atom to which the H-atom is attached.
The weighting scheme was calc w=1/[\s^2^(Fo^2^)+(0.0493P)^2^+6.8481P] where P=
Goodness-of-fit on F^2 was 1.070,
R1[for 13419 reflections with
I>2sigma(I)] = 0.0536, wR2 = 0.1387.
Data / restraints / parameters 16082/ 0/ 927.
Largest difference Fourier peak and hole 1.491 and -1.128 e.A^-3 .

Refinement used SHELXTL (Sheldrick, 1997).

We thank EPSRC and Siemens Analytical Instruments for grants in support
of the diffractometer.

Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

References

[ALCOCK, N.W. & MARKS, P.J. (1994), J. Appl. Cryst. 27, 200-200.]

COSIER, J. & GLAZER, A. M. (1986), J. Appl. Cryst. 19, 105-107.

SHELDRICK, G.M. (1990), Acta Cryst. A46, 467-473

SHELDRICK, G.M. (1993), Acta Cryst. D49, 18-23

SHELDRICK,G.M.(1997), SHELXTL Ver. 5.1, Bruker Analytical X-ray Systems, Madison, Wis. USA.

SIEMENS (1994), SMART User's manual, Siemens Industrial Automation Inc, Madison, Wis. USA.

Table 1. Crystal data and structure refinement for jul199m.

| | |
|---|---|
| Identification code | jul199m |
| Empirical formula | $C_{75}H_{82}Cl_2Cu_2F_6N_4O_6S_2$ |
| Formula weight | 1511.55 |
| Temperature | 180(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a$ = 11.4466(6) Å alpha = 69.3870(10)°<br>$b$ = 18.1140(9) Å beta = 78.2460(10)°<br>$c$ = 19.5085(6) Å gamma = 82.4430(10)° |
| Volume, Z | 3698.7(3) $Å^3$, 2 |
| Density (calculated) | 1.357 $Mg/m^3$ |
| Absorption coefficient | 0.772 $mm^{-1}$ |
| F(000) | 1572 |
| Crystal size | 0.60 x 0.40 x 0.40 mm |
| θ range for data collection | 1.13 to 28.48° |
| Limiting indices | $-14 \le h \le 15$, $-21 \le k \le 24$, $-17 \le l \le 26$ |
| Reflections collected | 22072 |
| Independent reflections | 16082 ($R_{int}$ = 0.0165) |
| Completeness to θ = 28.48° | 85.8 % |
| Absorption correction | SADABS |
| Max. and min. transmission | 0.9280 and 0.7373 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 16082 / 0 / 927 |
| Goodness-of-fit on $F^2$ | 1.070 |
| Final R indices [$I>2\sigma(I)$] | R1 = 0.0536, wR2 = 0.1247 |
| R indices (all data) | R1 = 0.0686, wR2 = 0.1387 |
| Largest diff. peak and hole | 1.491 and -1.128 $eÅ^{-3}$ |

Table 2. Atomic coordinates [ x $10^4$] and equivalent isotropic displacement parameters [$Å^2$ x $10^3$] for jul199m. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cu1 | 2653.5(3) | 2517.0(2) | 1755.8(2) | 27(1) |
| Cu2 | 1761.5(3) | 2764.7(2) | 3268.7(2) | 28(1) |
| N11 | 3711(2) | 1712.6(14) | 2293.0(12) | 26(1) |
| N12 | 2374.5(19) | 3773.1(13) | 2745.1(12) | 24(1) |
| N21 | 1433(2) | 3228.9(13) | 1303.9(12) | 25(1) |
| N22 | 915(2) | 1835.8(13) | 3685.5(12) | 26(1) |
| C101 | 3766(3) | 880.6(18) | 1541.1(16) | 33(1) |
| C102 | 3689(3) | 98.1(19) | 1611.9(19) | 42(1) |
| C103 | 3348(3) | -85(2) | 1051(2) | 45(1) |
| C104 | 3121(3) | 495(2) | 391.1(18) | 38(1) |
| C105 | 3249(3) | 1272(2) | 316.8(19) | 44(1) |
| C106 | 3564(3) | 1463.3(19) | 881.0(18) | 40(1) |
| C107 | 2732(3) | 282(3) | -218(2) | 51(1) |
| C108 | 3376(5) | -498(3) | -279(3) | 68(1) |
| C109 | 1399(5) | 184(6) | -7(4) | 128(3) |
| C110 | 3052(6) | 905(3) | -985(3) | 91(2) |
| C111 | 4048(3) | 1059.7(18) | 2159.3(16) | 33(1) |
| C112 | 4012(2) | 1788.2(17) | 2946.8(15) | 27(1) |
| C113 | 4045(3) | 1133.5(18) | 3593.0(16) | 34(1) |
| C114 | 4362(3) | 1221(2) | 4206.9(16) | 38(1) |
| C115 | 4619(3) | 1950.2(19) | 4190.0(16) | 35(1) |
| C116 | 4555(2) | 2617.1(18) | 3560.4(16) | 30(1) |
| C117 | 4250(2) | 2536.9(16) | 2925.5(15) | 25(1) |
| C118 | 4846(3) | 3406(2) | 3558.6(19) | 41(1) |
| C119 | 4289(2) | 3234.1(16) | 2228.2(14) | 25(1) |
| C120 | 5303(3) | 3317.7(18) | 1665.1(16) | 30(1) |
| C121 | 5376(3) | 4005.1(19) | 1046.1(16) | 36(1) |
| C122 | 4460(3) | 4592.9(18) | 969.6(16) | 35(1) |
| C123 | 3453(3) | 4510.0(17) | 1511.8(15) | 31(1) |
| C124 | 3383(2) | 3845.3(16) | 2151.3(14) | 24(1) |
| C125 | 6326(3) | 2698(2) | 1726.3(19) | 44(1) |
| C126 | 1853(3) | 4415.9(17) | 2835.8(15) | 29(1) |
| C127 | 801(3) | 4460.7(16) | 3385.8(16) | 29(1) |
| C128 | 55(3) | 5146.0(18) | 3232.5(18) | 38(1) |
| C129 | -980(3) | 5208(2) | 3723.8(18) | 42(1) |
| C130 | -1304(3) | 4603(2) | 4388.7(17) | 36(1) |
| C131 | -534(3) | 3927(2) | 4541.6(19) | 46(1) |
| C132 | 505(3) | 3855.0(19) | 4053.2(18) | 41(1) |
| C133 | -2465(3) | 4676(2) | 4916(2) | 47(1) |
| C134 | -2299(4) | 4268(4) | 5720(2) | 92(2) |
| C135 | -2899(5) | 5537(3) | 4807(3) | 87(2) |
| C136 | -3422(4) | 4280(4) | 4750(3) | 79(2) |
| C201 | 2259(3) | 3514.7(17) | -23.9(15) | 30(1) |
| C202 | 1875(3) | 3573(2) | -678.6(17) | 38(1) |
| C203 | 2691(3) | 3545(2) | -1298.4(17) | 39(1) |
| C204 | 3919(3) | 3485.6(19) | -1300.9(16) | 34(1) |
| C205 | 4297(3) | 3448.1(19) | -647.9(17) | 35(1) |
| C206 | 3486(3) | 3460.0(18) | -21.8(15) | 30(1) |

| | | | | |
|---|---|---|---|---|
| C207 | 4844(3) | 3460(2) | -1981.5(19) | 48(1) |
| C208 | 5743(5) | 4082(4) | -2165(2) | 87(2) |
| C209 | 5548(4) | 2642(4) | -1781(3) | 80(2) |
| C210 | 4283(4) | 3564(3) | -2653(2) | 64(1) |
| C211 | 1341(3) | 3538.5(17) | 605.7(15) | 30(1) |
| C212 | 411(2) | 3403.3(16) | 1804.3(15) | 26(1) |
| C213 | -5(3) | 4188.9(17) | 1683.7(17) | 34(1) |
| C214 | -991(3) | 4371.9(19) | 2148.2(19) | 41(1) |
| C215 | -1561(3) | 3773(2) | 2731.3(18) | 39(1) |
| C216 | -1164(3) | 2985.8(18) | 2866.4(16) | 31(1) |
| C217 | -149(2) | 2789.0(16) | 2404.4(15) | 26(1) |
| C218 | -1875(3) | 2364(2) | 3487.8(18) | 43(1) |
| C219 | 298(2) | 1948.0(16) | 2507.3(15) | 26(1) |
| C220 | 186(3) | 1582.5(17) | 1999.7(15) | 29(1) |
| C221 | 593(3) | 796.1(18) | 2127.2(17) | 36(1) |
| C222 | 1083(3) | 357.6(18) | 2752.5(18) | 38(1) |
| C223 | 1174(3) | 699.5(17) | 3271.8(16) | 33(1) |
| C224 | 780(2) | 1484.2(16) | 3148.3(15) | 26(1) |
| C225 | -397(3) | 2001(2) | 1325.4(17) | 38(1) |
| C226 | 404(3) | 1490.3(17) | 4360.2(15) | 31(1) |
| C227 | 486(3) | 1683.8(17) | 5011.1(15) | 30(1) |
| C228 | 1502(3) | 1956.6(17) | 5104.6(16) | 32(1) |
| C229 | 1534(3) | 2096.2(18) | 5757.2(17) | 35(1) |
| C230 | 551(3) | 1975.4(17) | 6331.2(16) | 33(1) |
| C231 | -475(3) | 1718.6(18) | 6220.7(16) | 34(1) |
| C232 | -502(3) | 1554.1(18) | 5585.0(16) | 34(1) |
| C233 | 546(4) | 2106(2) | 7064.6(18) | 43(1) |
| C234 | 1753(4) | 2336(3) | 7114(2) | 64(1) |
| C235 | 233(5) | 1345(2) | 7720.6(19) | 59(1) |
| C236 | -414(4) | 2767(2) | 7132(2) | 59(1) |
| S001 | 1664.8(7) | 6444.4(5) | 631.2(4) | 35(1) |
| S02A | 3975.6(12) | 8772.5(6) | 4029.2(9) | 36(1) |
| C02A | 4539(5) | 8050(4) | 3571(4) | 58(1) |
| O021 | 3337(3) | 8308(3) | 4727.0(18) | 53(1) |
| F021 | 5170(4) | 8383(4) | 2895(2) | 86(1) |
| S02B | 4526(5) | 8856(2) | 3614(3) | 44(2) |
| C02B | 4172(16) | 7819(10) | 4066(10) | 46(4) |
| F02B | 3489(10) | 7716(8) | 4722(5) | 62(3) |
| O02B | 5273(16) | 8884(12) | 2926(8) | 74(5) |
| O022 | 5066(3) | 9056.7(19) | 4077.9(17) | 69(1) |
| O023 | 3264(3) | 9301.4(16) | 3541.2(16) | 61(1) |
| F022 | 3632(3) | 7672(2) | 3537(2) | 99(1) |
| F023 | 5239(3) | 7459.9(18) | 4006(2) | 99(1) |
| O011 | 1107(3) | 6031.2(17) | 1374.1(15) | 58(1) |
| O012 | 2944(2) | 6343.0(16) | 497.9(15) | 49(1) |
| O013 | 1103(2) | 6393.5(15) | 57.1(15) | 49(1) |
| F011 | 1877(3) | 7948.3(14) | -101.9(13) | 75(1) |
| F012 | 1847(2) | 7631.2(15) | 1070.8(13) | 66(1) |
| F013 | 228(3) | 7686.9(17) | 660(2) | 86(1) |
| C001 | 1388(4) | 7478(2) | 560(2) | 49(1) |
| Cl01 | 7581.3(16) | 289.4(9) | 4385.4(11) | 108(1) |
| Cl02 | 7291.7(14) | 635.9(10) | 2828.5(11) | 119(1) |
| C003 | 7689(8) | -64(3) | 3667(4) | 125(3) |

**Table 3. Selected bond lengths [Å] and angles [°] for jul199m.**

| | | | |
|---|---|---|---|
| Cu1-N21 | 1.902(2) | Cu1-N11 | 1.914(2) |
| Cu2-N22 | 1.891(2) | Cu2-N12 | 1.898(2) |
| N21-Cu1-N11 | 172.26(10) | N22-Cu2-N12 | 169.22(10) |
| C111-N11-Cu1 | 123.6(2) | C112-N11-Cu1 | 117.97(18) |
| C126-N12-Cu2 | 123.07(19) | C124-N12-Cu2 | 118.92(17) |
| C211-N21-Cu1 | 129.3(2) | C212-N21-Cu1 | 116.01(17) |
| C226-N22-Cu2 | 130.4(2) | C224-N22-Cu2 | 113.83(17) |

Symmetry transformations used to generate equivalent atoms:

**Table 4. Bond lengths [Å] and angles [°] for jul199m.**

| | | | |
|---|---|---|---|
| Cu1-N21 | 1.902(2) | Cu1-N11 | 1.914(2) |
| Cu2-N22 | 1.891(2) | Cu2-N12 | 1.898(2) |
| N11-C111 | 1.293(4) | N11-C112 | 1.442(3) |
| N12-C126 | 1.290(4) | N12-C124 | 1.442(3) |
| N21-C211 | 1.298(3) | N21-C212 | 1.441(4) |
| N22-C226 | 1.292(4) | N22-C224 | 1.446(4) |
| C101-C106 | 1.388(4) | C101-C102 | 1.388(4) |
| C101-C111 | 1.458(4) | C102-C103 | 1.388(5) |
| C103-C104 | 1.393(5) | C104-C105 | 1.388(5) |
| C104-C107 | 1.530(5) | C105-C106 | 1.388(5) |
| C107-C109 | 1.514(6) | C107-C110 | 1.531(7) |
| C107-C108 | 1.537(6) | C112-C113 | 1.397(4) |
| C112-C117 | 1.403(4) | C113-C114 | 1.385(4) |
| C114-C115 | 1.377(5) | C115-C116 | 1.394(4) |
| C116-C117 | 1.412(4) | C116-C118 | 1.507(4) |
| C117-C119 | 1.493(4) | C119-C124 | 1.403(4) |
| C119-C120 | 1.410(4) | C120-C121 | 1.394(4) |
| C120-C125 | 1.504(4) | C121-C122 | 1.383(4) |
| C122-C123 | 1.381(4) | C123-C124 | 1.393(4) |
| C126-C127 | 1.455(4) | C127-C128 | 1.387(4) |
| C127-C132 | 1.388(4) | C128-C129 | 1.382(4) |
| C129-G130 | 1.390(5) | C130-C131 | 1.389(5) |
| C130-C133 | 1.528(4) | C131-C132 | 1.387(5) |
| C133-C134 | 1.520(6) | C133-C135 | 1.527(7) |
| C133-C136 | 1.528(6) | C201-C206 | 1.395(4) |
| C201-C202 | 1.399(4) | C201-C211 | 1.454(4) |
| C202-C203 | 1.381(4) | C203-C204 | 1.394(4) |
| C204-C205 | 1.404(4) | C204-C207 | 1.531(4) |
| C205-C206 | 1.381(4) | C207-C210 | 1.518(5) |
| C207-C208 | 1.526(5) | C207-C209 | 1.551(7) |
| C212-C213 | 1.393(4) | C212-C217 | 1.409(4) |
| C213-C214 | 1.378(5) | C214-C215 | 1.382(5) |
| C215-C216 | 1.388(4) | C216-C217 | 1.407(4) |
| C216-C218 | 1.509(4) | C217-C219 | 1.498(4) |
| C219-C220 | 1.404(4) | C219-C224 | 1.412(4) |
| C220-C221 | 1.390(4) | C220-C225 | 1.508(4) |
| C221-C222 | 1.384(4) | C222-C223 | 1.386(4) |
| C223-C224 | 1.384(4) | C226-C227 | 1.454(4) |
| C227-C228 | 1.389(4) | C227-C232 | 1.399(4) |
| C228-C229 | 1.391(4) | C229-C230 | 1.395(4) |
| C230-C231 | 1.400(4) | C230-C233 | 1.529(4) |
| C231-C232 | 1.380(4) | C233-C234 | 1.526(6) |
| C233-C236 | 1.538(5) | C233-C235 | 1.539(5) |
| S001-O011 | 1.433(3) | S001-O012 | 1.433(2) |
| S001-O013 | 1.435(2) | S001-C001 | 1.818(4) |
| S02A-O023 | 1.399(3) | S02A-O021 | 1.430(4) |
| S02A-O022 | 1.444(3) | S02A-C02A | 1.815(6) |
| C02A-F021 | 1.337(8) | C02A-F022 | 1.341(7) |
| C02A-F023 | 1.385(7) | S02B-O022 | 1.361(5) |
| S02B-O02B | 1.426(17) | S02B-O023 | 1.567(5) |
| S02B-C02B | 1.832(18) | C02B-F023 | 1.310(17) |
| C02B-F02B | 1.32(2) | C02B-F022 | 1.420(16) |
| F011-C001 | 1.328(4) | F012-C001 | 1.339(4) |
| F013-C001 | 1.326(5) | C101-C003 | 1.712(7) |
| C102-C003 | 1.783(6) | | |

| | | | |
|---|---|---|---|
| N21-Cu1-N11 | 172.26(10) | N22-Cu2-N12 | 169.22(10) |
| C111-N11-C112 | 117.8(2) | C111-N11-Cu1 | 123.6(2) |
| C112-N11-Cu1 | 117.97(18) | C126-N12-C124 | 117.5(2) |
| C126-N12-Cu2 | 123.07(19) | C124-N12-Cu2 | 118.92(17) |
| C211-N21-C212 | 114.5(2) | C211-N21-Cu1 | 129.3(2) |
| C212-N21-Cu1 | 116.01(17) | C226-N22-C224 | 115.7(2) |
| C226-N22-Cu2 | 130.4(2) | C224-N22-Cu2 | 113.83(17) |
| C106-C101-C102 | 118.3(3) | C106-C101-C111 | 122.6(3) |
| C102-C101-C111 | 119.1(3) | C101-C102-C103 | 120.2(3) |
| C102-C103-C104 | 122.0(3) | C105-C104-C103 | 117.0(3) |
| C105-C104-C107 | 121.7(3) | C103-C104-C107 | 121.2(3) |
| C106-C105-C104 | 121.4(3) | C101-C106-C105 | 120.9(3) |
| C109-C107-C104 | 107.5(3) | C109-C107-C110 | 111.7(5) |
| C104-C107-C110 | 111.9(3) | C109-C107-C108 | 109.0(5) |
| C104-C107-C108 | 111.0(3) | C110-C107-C108 | 105.8(4) |
| N11-C111-C101 | 124.2(3) | C113-C112-C117 | 120.6(3) |
| C113-C112-N11 | 120.8(3) | C117-C112-N11 | 118.6(2) |
| C114-C113-C112 | 119.5(3) | C115-C114-C113 | 120.6(3) |
| C114-C115-C116 | 121.0(3) | C115-C116-C117 | 119.2(3) |
| C115-C116-C118 | 119.7(3) | C117-C116-C118 | 121.1(3) |
| C112-C117-C116 | 119.1(2) | C112-C117-C119 | 121.4(2) |
| C116-C117-C119 | 119.3(2) | C124-C119-C120 | 119.1(2) |
| C124-C119-C117 | 121.0(2) | C120-C119-C117 | 119.6(2) |
| C121-C120-C119 | 119.0(3) | C121-C120-C125 | 119.1(3) |
| C119-C120-C125 | 121.8(3) | C122-C121-C120 | 121.1(3) |
| C123-C122-C121 | 120.3(3) | C122-C123-C124 | 119.7(3) |
| C123-C124-C119 | 120.7(2) | C123-C124-N12 | 120.5(2) |
| C119-C124-N12 | 118.9(2) | N12-C126-C127 | 125.3(3) |
| C128-C127-C132 | 118.4(3) | C128-C127-C126 | 118.1(3) |
| C132-C127-C126 | 123.6(3) | C129-C128-C127 | 120.4(3) |
| C128-C129-C130 | 122.1(3) | C131-C130-C129 | 116.8(3) |
| C131-C130-C133 | 121.9(3) | C129-C130-C133 | 121.3(3) |
| C132-C131-C130 | 121.8(3) | C131-C132-C127 | 120.5(3) |
| C134-C133-C135 | 108.7(4) | C134-C133-C130 | 110.6(3) |
| C135-C133-C130 | 112.1(3) | C134-C133-C136 | 109.4(4) |
| C135-C133-C136 | 108.2(4) | C130-C133-C136 | 107.9(3) |
| C206-C201-C202 | 118.4(3) | C206-C201-C211 | 124.4(3) |
| C202-C201-C211 | 117.2(3) | C203-C202-C201 | 120.7(3) |
| C202-C203-C204 | 121.3(3) | C203-C204-C205 | 117.6(3) |
| C203-C204-C207 | 122.5(3) | C205-C204-C207 | 119.9(3) |
| C206-C205-C204 | 121.4(3) | C205-C206-C201 | 120.5(3) |
| C210-C207-C208 | 110.8(4) | C210-C207-C204 | 112.9(3) |
| C208-C207-C204 | 109.7(3) | C210-C207-C209 | 107.8(4) |
| C208-C207-C209 | 107.1(4) | C204-C207-C209 | 108.2(3) |
| N21-C211-C201 | 126.7(3) | C213-C212-C217 | 120.9(3) |
| C213-C212-N21 | 118.7(2) | C217-C212-N21 | 120.4(2) |
| C214-C213-C212 | 119.9(3) | C213-C214-C215 | 119.7(3) |
| C214-C215-C216 | 121.6(3) | C215-C216-C217 | 119.4(3) |
| C215-C216-C218 | 118.4(3) | C217-C216-C218 | 122.1(3) |
| C216-C217-C212 | 118.4(3) | C216-C217-C219 | 121.8(2) |
| C212-C217-C219 | 119.7(2) | C220-C219-C224 | 118.0(3) |
| C220-C219-C217 | 121.6(2) | C224-C219-C217 | 120.4(2) |
| C221-C220-C219 | 119.4(3) | C221-C220-C225 | 117.8(3) |
| C219-C220-C225 | 122.7(3) | C222-C221-C220 | 121.5(3) |
| C221-C222-C223 | 120.1(3) | C224-C223-C222 | 118.9(3) |
| C223-C224-C219 | 122.0(3) | C223-C224-N22 | 118.0(2) |
| C219-C224-N22 | 119.9(2) | N22-C226-C227 | 126.6(3) |
| C228-C227-C232 | 118.7(3) | C228-C227-C226 | 123.7(3) |

| | | | |
|---|---|---|---|
| C232-C227-C226 | 117.5(3) | C227-C228-C229 | 120.5(3) |
| C228-C229-C230 | 121.3(3) | C229-C230-C231 | 117.4(3) |
| C229-C230-C233 | 123.5(3) | C231-C230-C233 | 119.1(3) |
| C232-C231-C230 | 121.6(3) | C231-C232-C227 | 120.3(3) |
| C234-C233-C230 | 112.4(3) | C234-C233-C236 | 109.3(3) |
| C230-C233-C236 | 108.3(3) | C234-C233-C235 | 107.9(3) |
| C230-C233-C235 | 110.0(3) | C236-C233-C235 | 108.9(3) |
| O011-S001-O012 | 114.84(17) | O011-S001-O013 | 114.98(17) |
| O012-S001-O013 | 114.57(16) | O011-S001-C001 | 103.55(18) |
| O012-S001-C001 | 103.12(18) | O013-S001-C001 | 103.54(16) |
| O023-S02A-O021 | 115.2(2) | O023-S02A-O022 | 116.8(2) |
| O021-S02A-O022 | 114.4(2) | O023-S02A-C02A | 102.4(3) |
| O021-S02A-C02A | 103.0(3) | O022-S02A-C02A | 102.0(3) |
| F021-C02A-F022 | 111.3(6) | F021-C02A-F023 | 110.1(5) |
| F022-C02A-F023 | 104.1(5) | F021-C02A-S02A | 111.6(5) |
| F022-C02A-S02A | 110.0(4) | F023-C02A-S02A | 109.5(4) |
| O022-S02B-O02B | 114.0(8) | O022-S02B-O023 | 111.4(4) |
| O02B-S02B-O023 | 114.8(7) | O022-S02B-C02B | 107.7(6) |
| O02B-S02B-C02B | 104.9(11) | O023-S02B-C02B | 103.0(6) |
| F023-C02B-F02B | 121.1(14) | F023-C02B-F022 | 103.9(12) |
| F02B-C02B-F022 | 115.1(13) | F023-C02B-S02B | 101.0(11) |
| F02B-C02B-S02B | 110.5(12) | F022-C02B-S02B | 102.9(10) |
| S02B-O022-S02A | 37.2(2) | S02A-O023-S02B | 34.65(18) |
| C02A-F022-C02B | 39.6(7) | C02B-F023-C02A | 40.7(8) |
| F013-C001-F011 | 107.7(3) | F013-C001-F012 | 107.0(3) |
| F011-C001-F012 | 107.3(3) | F013-C001-S001 | 111.8(3) |
| F011-C001-S001 | 111.2(3) | F012-C001-S001 | 111.6(2) |
| Cl01-C003-Cl02 | 115.5(3) | | |

Symmetry transformations used to generate equivalent atoms:

**Table 5. Anisotropic displacement parameters [$Å^2 \times 10^3$] for jul199m.**

**The anisotropic displacement factor exponent takes the form:**

$-2\pi^2 [ (ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12} ]$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cu1 | 28(1) | 29(1) | 22(1) | -6(1) | -7(1) | 4(1) |
| Cu2 | 33(1) | 25(1) | 22(1) | -5(1) | -1(1) | -7(1) |
| N11 | 27(1) | 27(1) | 24(1) | -9(1) | -6(1) | 2(1) |
| N12 | 21(1) | 28(1) | 23(1) | -9(1) | -1(1) | -2(1) |
| N21 | 25(1) | 26(1) | 23(1) | -4(1) | -5(1) | -4(1) |
| N22 | 28(1) | 25(1) | 21(1) | -4(1) | -5(1) | -3(1) |
| C101 | 37(2) | 31(2) | 30(2) | -13(1) | -9(1) | 7(1) |
| C102 | 57(2) | 30(2) | 39(2) | -10(1) | -15(2) | 6(1) |
| C103 | 57(2) | 35(2) | 49(2) | -16(2) | -15(2) | -3(2) |
| C104 | 34(2) | 45(2) | 39(2) | -18(1) | -8(1) | 1(1) |
| C105 | 57(2) | 41(2) | 34(2) | -12(1) | -14(2) | 8(2) |
| C106 | 55(2) | 28(2) | 35(2) | -12(1) | -8(1) | 4(1) |
| C107 | 45(2) | 70(3) | 48(2) | -29(2) | -14(2) | -5(2) |
| C108 | 82(3) | 74(3) | 64(3) | -42(2) | -14(2) | -11(2) |
| C109 | 44(3) | 260(10) | 137(6) | -133(7) | -15(3) | -20(4) |
| C110 | 150(6) | 85(4) | 54(3) | -29(3) | -44(3) | -9(4) |
| C111 | 36(2) | 33(2) | 30(1) | -9(1) | -11(1) | 6(1) |
| C112 | 24(1) | 32(1) | 24(1) | -7(1) | -6(1) | 3(1) |
| C113 | 36(2) | 31(2) | 30(1) | -4(1) | -9(1) | 1(1) |
| C114 | 37(2) | 42(2) | 24(1) | 0(1) | -9(1) | 5(1) |
| C115 | 32(2) | 47(2) | 26(1) | -12(1) | -10(1) | 2(1) |
| C116 | 25(1) | 38(2) | 27(1) | -12(1) | -6(1) | 2(1) |
| C117 | 21(1) | 30(1) | 23(1) | -7(1) | -4(1) | 2(1) |
| C118 | 43(2) | 47(2) | 43(2) | -21(2) | -16(1) | -3(2) |
| C119 | 25(1) | 26(1) | 23(1) | -8(1) | -4(1) | -3(1) |
| C120 | 27(1) | 36(2) | 26(1) | -11(1) | -1(1) | 0(1) |
| C121 | 34(2) | 42(2) | 27(1) | -11(1) | 4(1) | -4(1) |
| C122 | 45(2) | 31(2) | 23(1) | -4(1) | 2(1) | -5(1) |
| C123 | 34(2) | 27(1) | 27(1) | -6(1) | -4(1) | 2(1) |
| C124 | 25(1) | 26(1) | 23(1) | -9(1) | -1(1) | -4(1) |
| C125 | 28(2) | 55(2) | 38(2) | -11(2) | 1(1) | 10(1) |
| C126 | 30(1) | 27(1) | 28(1) | -8(1) | -1(1) | -4(1) |
| C127 | 29(1) | 26(1) | 31(1) | -11(1) | -1(1) | -1(1) |
| C128 | 42(2) | 28(2) | 34(2) | -7(1) | 6(1) | 2(1) |
| C129 | 39(2) | 39(2) | 40(2) | -12(1) | -3(1) | 12(1) |
| C130 | 30(2) | 47(2) | 34(2) | -21(1) | 2(1) | -3(1) |
| C131 | 57(2) | 37(2) | 33(2) | -7(1) | 10(2) | -3(2) |
| C132 | 49(2) | 31(2) | 34(2) | -7(1) | 2(1) | 8(1) |
| C133 | 31(2) | 70(2) | 41(2) | -24(2) | 5(1) | -5(2) |
| C134 | 56(3) | 168(6) | 43(2) | -40(3) | 6(2) | 12(3) |
| C135 | 63(3) | 96(4) | 103(4) | -59(3) | 28(3) | 3(3) |
| C136 | 36(2) | 128(5) | 84(3) | -55(3) | 7(2) | -23(2) |
| C201 | 30(1) | 33(2) | 22(1) | -2(1) | -3(1) | -4(1) |
| C202 | 28(2) | 52(2) | 29(2) | -6(1) | -8(1) | -3(1) |
| C203 | 36(2) | 54(2) | 26(1) | -9(1) | -7(1) | -9(1) |
| C204 | 32(2) | 40(2) | 29(1) | -10(1) | 0(1) | -10(1) |
| C205 | 28(1) | 44(2) | 33(2) | -10(1) | -4(1) | -10(1) |
| C206 | 29(1) | 36(2) | 24(1) | -4(1) | -7(1) | -8(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C207 | 39(2) | 71(2) | 38(2) | -25(2) | 6(1) | -23(2) |
| C208 | 91(4) | 131(5) | 47(2) | -38(3) | 27(2) | -76(4) |
| C209 | 55(3) | 116(4) | 77(3) | -52(3) | -5(2) | 16(3) |
| C210 | 56(2) | 107(4) | 35(2) | -34(2) | 2(2) | -15(2) |
| C211 | 27(1) | 30(1) | 27(1) | -3(1) | -7(1) | -2(1) |
| C212 | 24(1) | 29(1) | 24(1) | -6(1) | -8(1) | -1(1) |
| C213 | 39(2) | 27(1) | 33(2) | -3(1) | -10(1) | 1(1) |
| C214 | 46(2) | 32(2) | 43(2) | -13(1) | -12(2) | 11(1) |
| C215 | 34(2) | 42(2) | 39(2) | -17(1) | -3(1) | 7(1) |
| C216 | 27(1) | 38(2) | 28(1) | -10(1) | -3(1) | 0(1) |
| C217 | 25(1) | 27(1) | 23(1) | -5(1) | -6(1) | 1(1) |
| C218 | 31(2) | 53(2) | 35(2) | -9(2) | 3(1) | -2(1) |
| C219 | 25(1) | 26(1) | 24(1) | -5(1) | -1(1) | -3(1) |
| C220 | 30(1) | 31(1) | 23(1) | -7(1) | -3(1) | -6(1) |
| C221 | 45(2) | 33(2) | 34(2) | -14(1) | -6(1) | -7(1) |
| C222 | 46(2) | 26(1) | 41(2) | -10(1) | -8(1) | -1(1) |
| C223 | 40(2) | 26(1) | 28(1) | -1(1) | -8(1) | -3(1) |
| C224 | 28(1) | 25(1) | 23(1) | -4(1) | -3(1) | -5(1) |
| C225 | 41(2) | 44(2) | 31(2) | -13(1) | -13(1) | -3(1) |
| C226 | 34(2) | 29(1) | 26(1) | -4(1) | -6(1) | -6(1) |
| C227 | 35(2) | 28(1) | 22(1) | -1(1) | -5(1) | -6(1) |
| C228 | 32(2) | 32(2) | 25(1) | -1(1) | -4(1) | -7(1) |
| C229 | 37(2) | 32(2) | 33(2) | -5(1) | -11(1) | -6(1) |
| C230 | 43(2) | 28(1) | 26(1) | -4(1) | -7(1) | -4(1) |
| C231 | 38(2) | 34(2) | 26(1) | -6(1) | 1(1) | -6(1) |
| C232 | 34(2) | 36(2) | 28(1) | -4(1) | -3(1) | -11(1) |
| C233 | 64(2) | 38(2) | 29(2) | -12(1) | -9(2) | -8(2) |
| C234 | 83(3) | 74(3) | 44(2) | -23(2) | -19(2) | -23(2) |
| C235 | 97(3) | 51(2) | 29(2) | -7(2) | -15(2) | -12(2) |
| C236 | 85(3) | 49(2) | 48(2) | -24(2) | -7(2) | -1(2) |
| S001 | 28(1) | 35(1) | 35(1) | -4(1) | -7(1) | -1(1) |
| S02A | 39(1) | 35(1) | 31(1) | -5(1) | -12(1) | -2(1) |
| C02A | 49(3) | 58(3) | 65(4) | -23(3) | -9(3) | 8(3) |
| O021 | 42(2) | 74(3) | 34(2) | -5(2) | -6(1) | -9(2) |
| F021 | 74(3) | 121(4) | 57(2) | -40(3) | 8(2) | 10(3) |
| S02B | 52(3) | 38(2) | 33(3) | 3(2) | -14(2) | -4(2) |
| C02B | 52(9) | 42(8) | 47(10) | -18(7) | -16(8) | -2(7) |
| F02B | 64(7) | 66(8) | 44(5) | -6(5) | 6(5) | -17(6) |
| O02B | 88(11) | 85(12) | 31(6) | -2(7) | 0(6) | -11(10) |
| O022 | 83(2) | 72(2) | 57(2) | -7(2) | -21(2) | -40(2) |
| O023 | 71(2) | 49(2) | 55(2) | -9(1) | -21(1) | 14(1) |
| F022 | 96(2) | 96(2) | 142(3) | -80(2) | -27(2) | -16(2) |
| F023 | 85(2) | 73(2) | 134(3) | -38(2) | -29(2) | 40(2) |
| O011 | 57(2) | 55(2) | 44(1) | 1(1) | 7(1) | -10(1) |
| O012 | 28(1) | 62(2) | 56(2) | -17(1) | -10(1) | 1(1) |
| O013 | 46(1) | 48(1) | 60(2) | -19(1) | -23(1) | -2(1) |
| F011 | 128(2) | 44(1) | 52(1) | 6(1) | -39(2) | -30(1) |
| F012 | 91(2) | 66(2) | 54(1) | -26(1) | -29(1) | -8(1) |
| F013 | 68(2) | 69(2) | 139(3) | -56(2) | -44(2) | 33(1) |
| C001 | 59(2) | 43(2) | 48(2) | -14(2) | -22(2) | 1(2) |
| Cl01 | 100(1) | 66(1) | 139(2) | -15(1) | 1(1) | -29(1) |
| Cl02 | 69(1) | 88(1) | 139(2) | 23(1) | 2(1) | -1(1) |
| C003 | 183(8) | 43(3) | 98(5) | 3(3) | 14(5) | 34(4) |

Table 6. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for jul199m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H10A | 3871 | -313 | 2046 | 50 |
| H10B | 3268 | -623 | 1118 | 54 |
| H10C | 3117 | 1682 | -130 | 53 |
| H10D | 3644 | 2001 | 814 | 47 |
| H10E | 3152 | -930 | 186 | 101 |
| H10F | 4243 | -454 | -374 | 101 |
| H10G | 3145 | -607 | -690 | 101 |
| H10H | 1233 | -240 | 472 | 192 |
| H10I | 1121 | 49 | -389 | 192 |
| H10J | 982 | 679 | 32 | 192 |
| H11A | 2587 | 1402 | -998 | 136 |
| H11B | 2867 | 722 | -1365 | 136 |
| H11C | 3908 | 988 | -1083 | 136 |
| H11D | 4510 | 671 | 2485 | 40 |
| H11E | 3850 | 632 | 3611 | 40 |
| H11F | 4404 | 775 | 4643 | 45 |
| H11G | 4842 | 1999 | 4614 | 42 |
| H11H | 5217 | 3328 | 3992 | 62 |
| H11I | 4109 | 3746 | 3580 | 62 |
| H11J | 5400 | 3656 | 3103 | 62 |
| H12A | 6066 | 4071 | 671 | 43 |
| H12B | 4524 | 5056 | 542 | 42 |
| H12C | 2811 | 4904 | 1449 | 37 |
| H12D | 6981 | 2892 | 1312 | 66 |
| H12E | 6058 | 2214 | 1709 | 66 |
| H12F | 6606 | 2586 | 2198 | 66 |
| H12G | 2182 | 4899 | 2518 | 35 |
| H12H | 255 | 5576 | 2787 | 45 |
| H12I | -1485 | 5679 | 3603 | 50 |
| H13A | -724 | 3503 | 4993 | 55 |
| H13B | 1017 | 3387 | 4176 | 50 |
| H13C | -1627 | 4483 | 5813 | 137 |
| H13D | -2134 | 3699 | 5816 | 137 |
| H13E | -3030 | 4359 | 6051 | 137 |
| H13F | -2273 | 5812 | 4878 | 131 |
| H13G | -3621 | 5559 | 5171 | 131 |
| H13H | -3080 | 5794 | 4304 | 131 |
| H13I | -3572 | 4567 | 4244 | 118 |
| H13J | -4162 | 4287 | 5104 | 118 |
| H13K | -3145 | 3732 | 4796 | 118 |
| H20A | 1043 | 3633 | -697 | 45 |
| H20B | 2411 | 3568 | -1732 | 47 |
| H20C | 5129 | 3414 | -637 | 42 |
| H20D | 3765 | 3431 | 414 | 36 |
| H20E | 5333 | 4610 | -2310 | 130 |
| H20F | 6369 | 4036 | -2576 | 130 |
| H20G | 6103 | 4000 | -1727 | 130 |
| H20H | 5003 | 2227 | -1677 | 121 |
| H20I | 5904 | 2555 | -1340 | 121 |

| | | | | |
|---|---|---|---|---|
| H20J | 6182 | 2627 | -2198 | 121 |
| H21A | 3829 | 4077 | -2791 | 96 |
| H21B | 3744 | 3141 | -2533 | 96 |
| H21C | 4913 | 3541 | -3070 | 96 |
| H21D | 597 | 3808 | 495 | 36 |
| H21E | 389 | 4598 | 1282 | 41 |
| H21F | -1277 | 4907 | 2068 | 49 |
| H21G | -2241 | 3905 | 3047 | 47 |
| H21H | -2725 | 2469 | 3448 | 64 |
| H21I | -1761 | 2379 | 3967 | 64 |
| H21J | -1600 | 1841 | 3452 | 64 |
| H22A | 532 | 554 | 1777 | 44 |
| H22B | 1359 | -178 | 2826 | 46 |
| H22C | 1501 | 400 | 3705 | 40 |
| H22D | -1004 | 1674 | 1311 | 57 |
| H22E | 209 | 2090 | 875 | 57 |
| H22F | -777 | 2510 | 1352 | 57 |
| H22G | -73 | 1067 | 4439 | 37 |
| H22H | 2180 | 2049 | 4720 | 38 |
| H22I | 2239 | 2277 | 5813 | 42 |
| H23A | -1170 | 1656 | 6592 | 41 |
| H23B | -1194 | 1352 | 5537 | 41 |
| H23C | 2358 | 1903 | 7101 | 95 |
| H23D | 1694 | 2442 | 7579 | 95 |
| H23E | 1984 | 2812 | 6692 | 95 |
| H23F | -569 | 1208 | 7724 | 89 |
| H23G | 251 | 1429 | 8188 | 89 |
| H23H | 817 | 913 | 7668 | 89 |
| H23I | -1204 | 2597 | 7157 | 89 |
| H23J | -253 | 3244 | 6697 | 89 |
| H23K | -396 | 2883 | 7584 | 89 |
| H00A | 7168 | -512 | 3832 | 150 |
| H00B | 8522 | -274 | 3556 | 150 |

**Table 7. Selected torsion angles [°] for jul199m.**

| | |
|---|---|
| N21-Cu1-N11-C111 | 79.2(8) |
| N21-Cu1-N11-C112 | -91.8(8) |
| N22-Cu2-N12-C126 | 67.1(6) |
| N22-Cu2-N12-C124 | -104.7(5) |
| N11-Cu1-N21-C211 | -126.8(7) |
| N11-Cu1-N21-C212 | 47.4(8) |
| N12-Cu2-N22-C226 | -116.0(5) |
| N12-Cu2-N22-C224 | 60.8(6) |

**Symmetry transformations used to generate equivalent atoms:**

**Table 8. Torsion angles [°] for jul199m.**

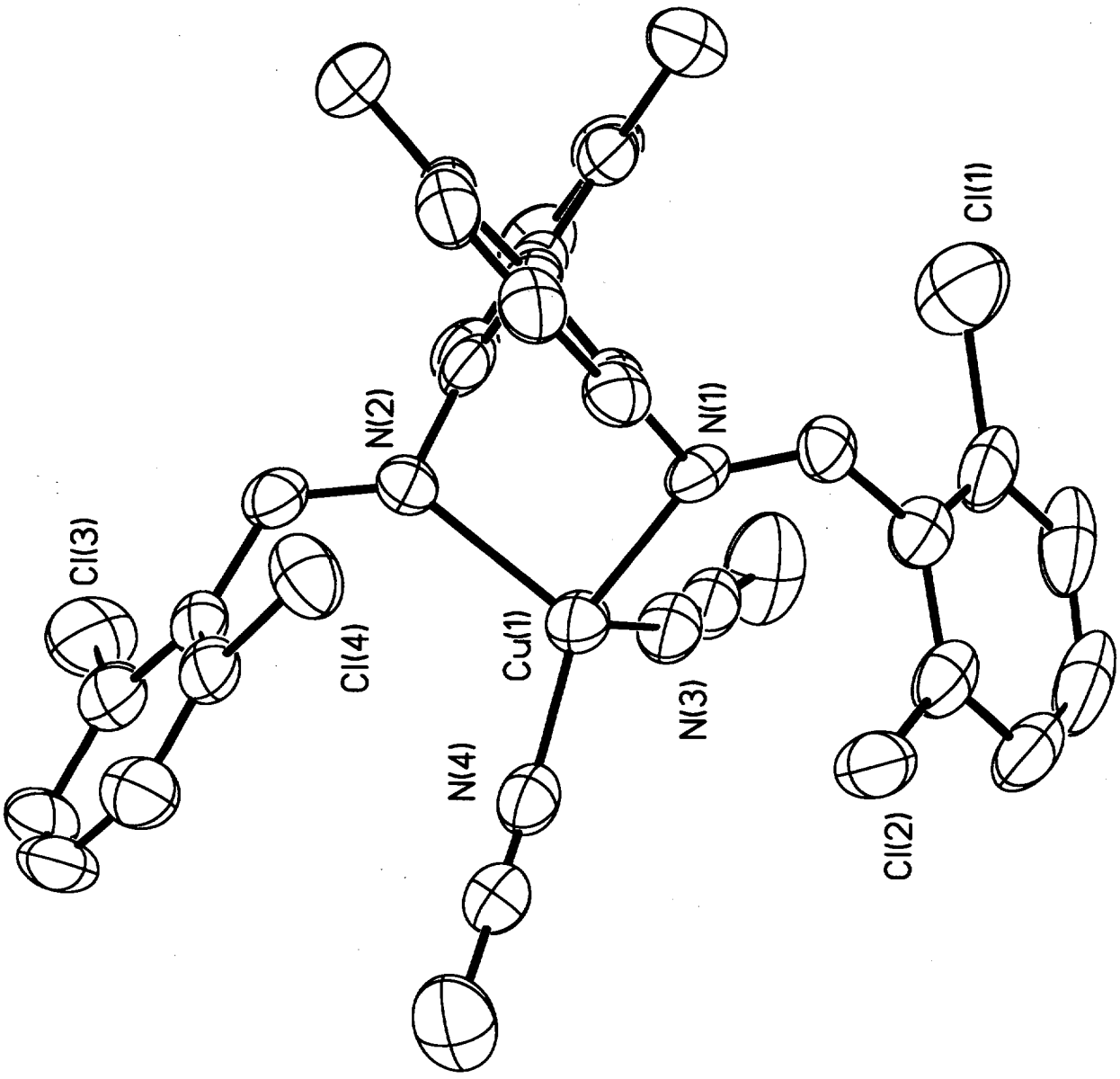
| | |
|---|---|
| N21-Cu1-N11-C111 | 79.2(8) |
| N21-Cu1-N11-C112 | -91.8(8) |
| N22-Cu2-N12-C126 | 67.1(6) |
| N22-Cu2-N12-C124 | -104.7(5) |
| N11-Cu1-N21-C211 | -126.8(7) |
| N11-Cu1-N21-C212 | 47.4(8) |
| N12-Cu2-N22-C226 | -116.0(5) |
| N12-Cu2-N22-C224 | 60.8(6) |
| C106-C101-C102-C103 | -3.8(5) |
| C111-C101-C102-C103 | 176.0(3) |
| C101-C102-C103-C104 | 2.7(6) |
| C102-C103-C104-C105 | 0.0(5) |
| C102-C103-C104-C107 | -179.3(3) |
| C103-C104-C105-C106 | -1.3(5) |
| C107-C104-C105-C106 | 177.9(3) |
| C102-C101-C106-C105 | 2.5(5) |
| C111-C101-C106-C105 | -177.3(3) |
| C104-C105-C106-C101 | 0.1(6) |
| C105-C104-C107-C109 | -97.3(5) |
| C103-C104-C107-C109 | 82.0(6) |
| C105-C104-C107-C110 | 25.7(5) |
| C103-C104-C107-C110 | -155.1(4) |
| C105-C104-C107-C108 | 143.6(4) |
| C103-C104-C107-C108 | -37.1(5) |
| C112-N11-C111-C101 | 177.1(3) |
| Cu1-N11-C111-C101 | 6.1(4) |
| C106-C101-C111-N11 | 27.7(5) |
| C102-C101-C111-N11 | -152.1(3) |
| C111-N11-C112-C113 | -34.3(4) |
| Cu1-N11-C112-C113 | 137.3(2) |
| C111-N11-C112-C117 | 147.0(3) |
| Cu1-N11-C112-C117 | -41.5(3) |
| C117-C112-C113-C114 | -2.7(4) |
| N11-C112-C113-C114 | 178.6(3) |
| C112-C113-C114-C115 | 1.5(5) |
| C113-C114-C115-C116 | 0.6(5) |
| C114-C115-C116-C117 | -1.5(4) |
| C114-C115-C116-C118 | -179.8(3) |
| C113-C112-C117-C116 | 1.7(4) |
| N11-C112-C117-C116 | -179.5(2) |
| C113-C112-C117-C119 | 176.5(3) |
| N11-C112-C117-C119 | -4.8(4) |
| C115-C116-C117-C112 | 0.3(4) |
| C118-C116-C117-C112 | 178.6(3) |
| C115-C116-C117-C119 | -174.5(3) |
| C118-C116-C117-C119 | 3.7(4) |
| C112-C117-C119-C124 | 108.8(3) |
| C116-C117-C119-C124 | -76.5(3) |
| C112-C117-C119-C120 | -77.1(3) |
| C116-C117-C119-C120 | 97.6(3) |
| C124-C119-C120-C121 | -0.2(4) |
| C117-C119-C120-C121 | -174.3(3) |
| C124-C119-C120-C125 | 177.7(3) |
| C117-C119-C120-C125 | 3.6(4) |
| C119-C120-C121-C122 | -1.6(5) |

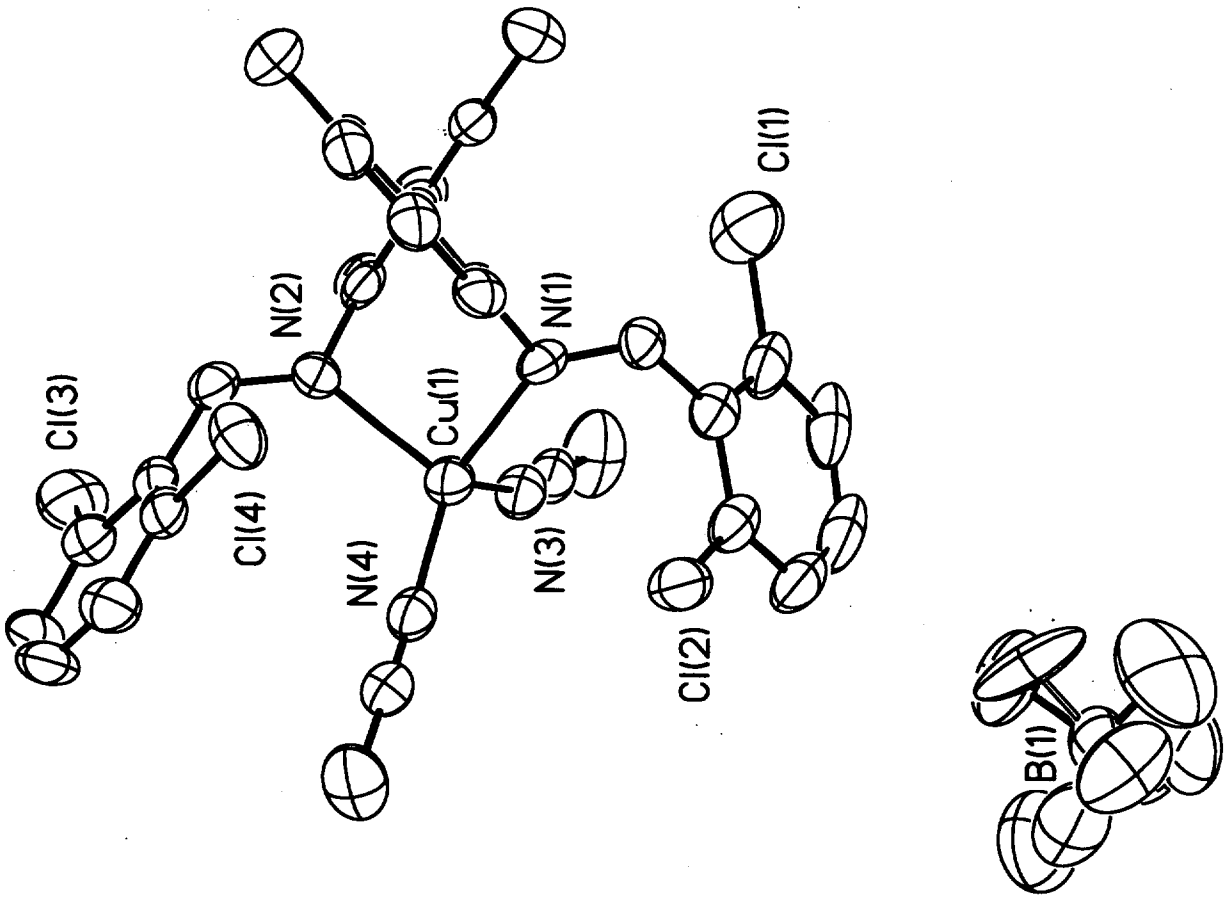
| | |
|---|---|
| C125-C120-C121-C122 | -179.5(3) |
| C120-C121-C122-C123 | 0.4(5) |
| C121-C122-C123-C124 | 2.5(5) |
| C122-C123-C124-C119 | -4.3(4) |
| C122-C123-C124-N12 | 175.9(3) |
| C120-C119-C124-C123 | 3.1(4) |
| C117-C119-C124-C123 | 177.2(3) |
| C120-C119-C124-N12 | -177.1(2) |
| C117-C119-C124-N12 | -3.0(4) |
| C126-N12-C124-C123 | -29.9(4) |
| Cu2-N12-C124-C123 | 142.5(2) |
| C126-N12-C124-C119 | 150.3(3) |
| Cu2-N12-C124-C119 | -37.3(3) |
| C124-N12-C126-C127 | 177.7(3) |
| Cu2-N12-C126-C127 | 5.7(4) |
| N12-C126-C127-C128 | -153.0(3) |
| N12-C126-C127-C132 | 26.8(5) |
| C132-C127-C128-C129 | -2.3(5) |
| C126-C127-C128-C129 | 177.6(3) |
| C127-C128-C129-C130 | 1.1(5) |
| C128-C129-C130-C131 | 0.3(5) |
| C128-C129-C130-C133 | -178.7(3) |
| C129-C130-C131-C132 | -0.5(5) |
| C133-C130-C131-C132 | 178.4(3) |
| C130-C131-C132-C127 | -0.6(6) |
| C128-C127-C132-C131 | 2.0(5) |
| C126-C127-C132-C131 | -177.8(3) |
| C131-C130-C133-C134 | 36.0(5) |
| C129-C130-C133-C134 | -145.1(4) |
| C131-C130-C133-C135 | 157.5(4) |
| C129-C130-C133-C135 | -23.6(5) |
| C131-C130-C133-C136 | -83.6(5) |
| C129-C130-C133-C136 | 95.3(4) |
| C206-C201-C202-C203 | 2.6(5) |
| C211-C201-C202-C203 | -179.2(3) |
| C201-C202-C203-C204 | -2.2(5) |
| C202-C203-C204-C205 | 0.5(5) |
| C202-C203-C204-C207 | -179.5(3) |
| C203-C204-C205-C206 | 0.8(5) |
| C207-C204-C205-C206 | -179.2(3) |
| C204-C205-C206-C201 | -0.4(5) |
| C202-C201-C206-C205 | -1.3(5) |
| C211-C201-C206-C205 | -179.4(3) |
| C203-C204-C207-C210 | 4.0(5) |
| C205-C204-C207-C210 | -176.0(3) |
| C203-C204-C207-C208 | 128.1(4) |
| C205-C204-C207-C208 | -51.9(5) |
| C203-C204-C207-C209 | -115.4(4) |
| C205-C204-C207-C209 | 64.7(4) |
| C212-N21-C211-C201 | 175.0(3) |
| Cu1-N21-C211-C201 | -10.7(4) |
| C206-C201-C211-N21 | -28.1(5) |
| C202-C201-C211-N21 | 153.8(3) |
| C211-N21-C212-C213 | -52.4(3) |
| Cu1-N21-C212-C213 | 132.6(2) |
| C211-N21-C212-C217 | 127.9(3) |
| Cu1-N21-C212-C217 | -47.2(3) |
| C217-C212-C213-C214 | -1.1(4) |
| N21-C212-C213-C214 | 179.2(3) |

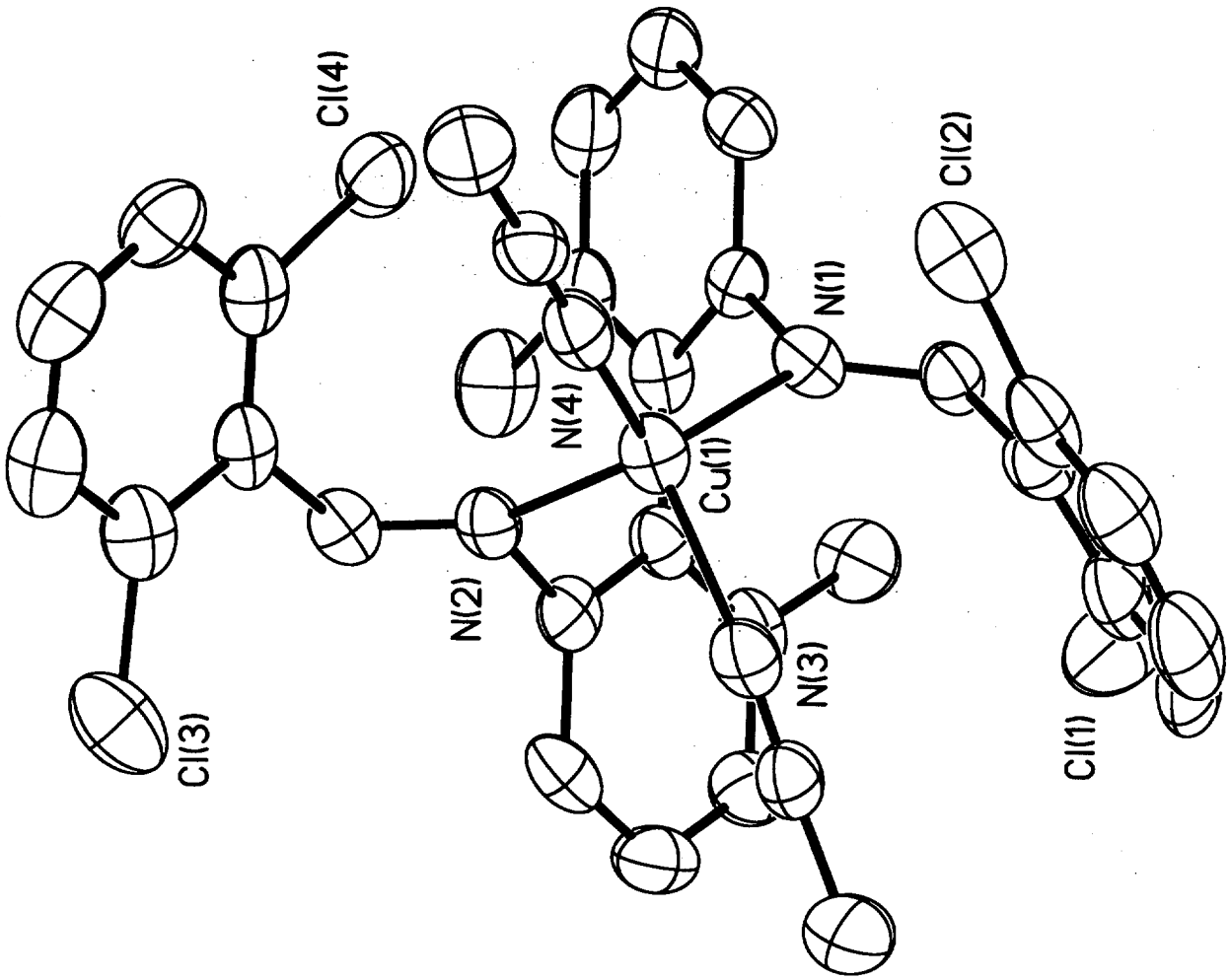
| | |
|---|---|
| C212-C213-C214-C215 | -0.1(5) |
| C213-C214-C215-C216 | 0.3(5) |
| C214-C215-C216-C217 | 0.7(5) |
| C214-C215-C216-C218 | -176.7(3) |
| C215-C216-C217-C212 | -1.8(4) |
| C218-C216-C217-C212 | 175.5(3) |
| C215-C216-C217-C219 | -178.0(3) |
| C218-C216-C217-C219 | -0.7(4) |
| C213-C212-C217-C216 | 2.0(4) |
| N21-C212-C217-C216 | -178.3(2) |
| C213-C212-C217-C219 | 178.3(3) |
| N21-C212-C217-C219 | -2.0(4) |
| C216-C217-C219-C220 | 108.8(3) |
| C212-C217-C219-C220 | -67.3(4) |
| C216-C217-C219-C224 | -67.1(4) |
| C212-C217-C219-C224 | 116.7(3) |
| C224-C219-C220-C221 | -2.6(4) |
| C217-C219-C220-C221 | -178.7(3) |
| C224-C219-C220-C225 | 175.4(3) |
| C217-C219-C220-C225 | -0.7(4) |
| C219-C220-C221-C222 | 1.4(5) |
| C225-C220-C221-C222 | -176.7(3) |
| C220-C221-C222-C223 | 0.3(5) |
| C221-C222-C223-C224 | -0.8(5) |
| C222-C223-C224-C219 | -0.6(4) |
| C222-C223-C224-N22 | -178.2(3) |
| C220-C219-C224-C223 | 2.3(4) |
| C217-C219-C224-C223 | 178.4(3) |
| C220-C219-C224-N22 | 179.8(2) |
| C217-C219-C224-N22 | -4.1(4) |
| C226-N22-C224-C223 | -57.7(4) |
| Cu2-N22-C224-C223 | 125.0(2) |
| C226-N22-C224-C219 | 124.6(3) |
| Cu2-N22-C224-C219 | -52.7(3) |
| C224-N22-C226-C227 | 174.6(3) |
| Cu2-N22-C226-C227 | -8.7(5) |
| N22-C226-C227-C228 | -33.8(5) |
| N22-C226-C227-C232 | 149.0(3) |
| C232-C227-C228-C229 | 0.1(4) |
| C226-C227-C228-C229 | -177.1(3) |
| C227-C228-C229-C230 | -0.6(5) |
| C228-C229-C230-C231 | -0.9(4) |
| C228-C229-C230-C233 | 178.9(3) |
| C229-C230-C231-C232 | 3.0(4) |
| C233-C230-C231-C232 | -176.8(3) |
| C230-C231-C232-C227 | -3.6(5) |
| C228-C227-C232-C231 | 2.0(4) |
| C226-C227-C232-C231 | 179.3(3) |
| C229-C230-C233-C234 | -3.3(5) |
| C231-C230-C233-C234 | 176.5(3) |
| C229-C230-C233-C236 | 117.5(4) |
| C231-C230-C233-C236 | -62.7(4) |
| C229-C230-C233-C235 | -123.6(4) |
| C231-C230-C233-C235 | 56.2(4) |
| O023-S02A-C02A-F021 | 60.0(5) |
| O021-S02A-C02A-F021 | 179.9(4) |
| O022-S02A-C02A-F021 | -61.3(5) |
| O023-S02A-C02A-F022 | -64.1(5) |
| O021-S02A-C02A-F022 | 55.8(5) |

| | |
|---|---|
| O022-S02A-C02A-F022 | 174.7(4) |
| O023-S02A-C02A-F023 | -177.9(4) |
| O021-S02A-C02A-F023 | -58.0(4) |
| O022-S02A-C02A-F023 | 60.9(5) |
| O022-S02B-C02B-F023 | -72.1(11) |
| O02B-S02B-C02B-F023 | 49.6(12) |
| O023-S02B-C02B-F023 | 170.1(8) |
| O022-S02B-C02B-F02B | 57.3(12) |
| O02B-S02B-C02B-F02B | 179.1(12) |
| O023-S02B-C02B-F02B | -60.5(11) |
| O022-S02B-C02B-F022 | -179.3(8) |
| O02B-S02B-C02B-F022 | -57.6(12) |
| O023-S02B-C02B-F022 | 62.9(11) |
| O02B-S02B-O022-S02A | -175.6(9) |
| O023-S02B-O022-S02A | 52.6(3) |
| C02B-S02B-O022-S02A | -59.6(7) |
| O023-S02A-O022-S02B | -68.3(3) |
| O021-S02A-O022-S02B | 152.8(4) |
| C02A-S02A-O022-S02B | 42.4(4) |
| O021-S02A-O023-S02B | -162.4(4) |
| O022-S02A-O023-S02B | 59.1(3) |
| C02A-S02A-O023-S02B | -51.4(3) |
| O022-S02B-O023-S02A | -60.7(4) |
| O02B-S02B-O023-S02A | 167.9(10) |
| C02B-S02B-O023-S02A | 54.5(6) |
| F021-C02A-F022-C02B | 177.6(13) |
| F023-C02A-F022-C02B | 59.0(11) |
| S02A-C02A-F022-C02B | -58.2(11) |
| F023-C02B-F022-C02A | -64.9(12) |
| F02B-C02B-F022-C02A | 160(2) |
| S02B-C02B-F022-C02A | 40.1(7) |
| F02B-C02B-F023-C02A | -170(2) |
| F022-C02B-F023-C02A | 59.2(10) |
| S02B-C02B-F023-C02A | -47.3(9) |
| F021-C02A-F023-C02B | 175.1(13) |
| F022-C02A-F023-C02B | -65.5(11) |
| S02A-C02A-F023-C02B | 52.1(11) |
| O011-S001-C001-F013 | -60.8(3) |
| O012-S001-C001-F013 | 179.2(3) |
| O013-S001-C001-F013 | 59.5(3) |
| O011-S001-C001-F011 | 178.7(3) |
| O012-S001-C001-F011 | 58.7(3) |
| O013-S001-C001-F011 | -61.0(3) |
| O011-S001-C001-F012 | 58.9(3) |
| O012-S001-C001-F012 | -61.1(3) |
| O013-S001-C001-F012 | 179.3(3) |

Symmetry transformations used to generate equivalent atoms:


Cl(1)
N(2)
N(1)
Cl(3)
Cl(4)
Cu(1)
N(3)
N(4)
Cl(2)


Cl(1)
N(2)
N(1)
Cl(3)
Cu(1)
Cl(4)
N(4)
N(3)
Cl(2)
B(1)


Cl(4)
Cl(2)
N(1)
N(4)
Cu(1)
N(2)
N(3)
Cl(3)
Cl(1)

Experimental data for cudo

Crystal Data

C34 H26 B Cl8 Cu F4 N4, M = 924.54, Orthorhombic, space group Pbca
a = 13.2095(5), b = 23.9347(5), c = 25.5398(10) A ,
alpha = 90 deg., beta = 90 deg., gamma = 90 deg.,
U = 8074.8(5) A^3 (by least squares refinement on 16689 reflection positions),
T =183(2)K, lambda = 0.71073 A, Z = 8,
D(cal) = 1.521 Mg/m^3, F(000) = 3712.
mu(MoK-alpha) = 1.120 mm^-1.
Crystal character:Yellow Block.
Crystal dimensions 0.60 x 0.30 x 0.30 mm,

Data Collection and Processing.

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector.
The crystal was held at 183(2)
K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986).
Maximum theta was 22.50 deg.
The hkl ranges were -14/ 13, -25/ 25, -27/ 25.
30543 reflections measured, 5276 unique [R(int) = 0.0537].
Absorption correction by SADABS;
minimum and maximum transmission factors: 0.5205;
0.9280.

no crystal decay

Structure Analysis and Refinement.

Systematic absences indicated space group Pbca
and shown to be correct by successful refinement.

The structure was solved by direct methods
using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by
Fourier methods.

Hydrogen atoms were added at calculated positions and refined using a riding
model with freely rotating methyl groups. Anisotropic displacement
parameters were used for all non-H atoms;
H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for
methyl hydrogen atoms) times the equivalent isotropic displacement parameter
of the atom to which the H-atom is attached.
Floating origin constraints were generated automatically.
The weighting scheme was calc w=1/[\s^2^(Fo^2^)+(0.1000P)^2^+0.0000P] where P=
Goodness-of-fit on F^2 was 2.131,
R1[for 4473 reflections with
I>2sigma(I)] = 0.0895, wR2 = 0.2723.
Data / restraints / parameters 5276/ 0/ 511.
Largest difference Fourier peak and hole 0.877 and -1.060 e.A^-3 .

Refinement used SHELXL 96 (Sheldrick, 1996).

We thank EPSRC and Siemens Analytical Instruments for grants in support
of the diffractometer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

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SHELDRICK,G.M.(1996), SHELX-96 (beta-test) (including SHELXS and SHELXL)

SIEMENS (1994), SMART User's manual, Siemens Industrial Automation Inc, Madison, Wis. USA.

Table 1. Crystal data and structure refinement for cudo.

| | |
|---|---|
| Identification code | cudo |
| Empirical formula | $C_{34}H_{26}BCl_8CuF_4N_4$ |
| Formula weight | 924.54 |
| Temperature | 183(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| Unit cell dimensions | a = 13.2095(5) Å alpha = 90°<br>b = 23.9347(5) Å beta = 90°<br>c = 25.5398(10) Å gamma = 90° |
| Volume, Z | 8074.8(5) $Å^3$, 8 |
| Density (calculated) | 1.521 $Mg/m^3$ |
| Absorption coefficient | 1.120 $mm^{-1}$ |
| F(000) | 3712 |
| Crystal size | 0.60 x 0.30 x 0.30 mm |
| θ range for data collection | 1.59 to 22.50° |
| Limiting indices | $-14 \le h \le 13$, $-25 \le k \le 25$, $-27 \le l \le 25$ |
| Reflections collected | 30543 |
| Independent reflections | 5276 ($R_{int}$ = 0.0537) |
| Completeness to θ = 22.50° | 99.8 % |
| Absorption correction | SADABS |
| Max. and min. transmission | 0.9280 and 0.5205 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5276 / 0 / 511 |
| Goodness-of-fit on $F^2$ | 2.131 |
| Final R indices [I>2σ(I)] | R1 = 0.0895, wR2 = 0.2640 |
| R indices (all data) | R1 = 0.1020, wR2 = 0.2723 |
| Largest diff. peak and hole | 0.877 and -1.060 $eÅ^{-3}$ |