Supramolecular Assembly in a Janus-Type Urea System

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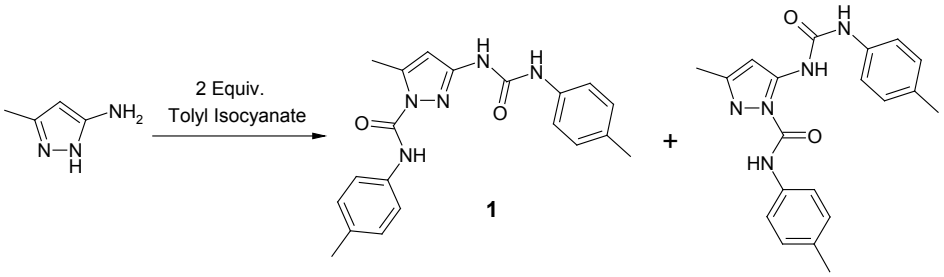
Supplementary Information

Synthesis



Scheme S1 Synthesis of **1** and its regioisomer.

Synthesis of 1: 3-amino-5-methylpyrazole (1.00 g, 10.3 mmol) was added to dry $CHCl_3$ (100 mL) in a three necked round bottom flask fitted with a condenser and flowing N_2. To this solution was added *p*-tolyl isocyanate (2.74 g, 2.60 ml, 20.6 mmol) dropwise. The solution was refluxed for 24 hours under N_2. The solvent was removed using a rotary evaporator to give a crystalline solid of a mixture of isomers. Compound 1-(1-(*p*-tolylcarbamoyl)-5-methyl-1*H*-pyrazol-3-yl)-3-*p*-tolylurea (**1**) was isolated by crystallisation from hot $CHCl_3$ and the crystalline material filtered hot. Solid was washed with hot $CHCl_3$ (15 ml). **Yield:** 0.79 g; 33%, 0.34 mmol. **^{1}H NMR:** (400 MHz, *d6*-DMSO, δ/ppm, *J*/Hz) 2.22 (3H, singlet, -CH_3) 2.51 (3H, singlet, -CH_3) 3.32 (3H, singlet, -CH_3) 6.44 (1H, singlet, =CH-) 7.08 (2H, doublet, J = 6.4; -CH=(tolyl)) 7.14 (2H, doublet, J = 7.2; -CH=(tolyl)) 7.34 (2H, doublet, J = 6.4; -CH=(tolyl)) 7.53 (2H, doublet, J = 7.2; -CH=(tolyl)) 8.99 (1H, singlet, -NH-) 9.12 (1H, singlet, -NH-) 9.81 (1H, singlet, -NH-). **^{13}C NMR:** (100 MHz, *d6*-DMSO, δ/ppm) 13.8, 20.3, 20.4, 101.4, 118.4, 121.2, 129.0, 129.1, 131.2, 133.0, 134.5, 136.5, 143.2, 148.4, 148.6, 151.7. **Elemental analysis:** Calc. C 65.9% H 5.93% N 19.2% Exp. C 66.1% H 5.82% N 19.3%. **Melting point:** 158 +/- 2 °C. **Mass Spectra:** ES^+ m/z = 231 [100%] $C_{20}H_{21}N_5O_2 - C_8H_7N_4O_1 + H^+$, m/z = 364 [34%] $C_{20}H_{21}N_5O_2 + H^+$, m/z = 386 [78%] $C_{20}H_{21}N_5O_2 + Na^+$, m/z = 749 [45%] $2C_{20}H_{21}N_5O_2 + Na^+$. **FT-IR:** ($v$, cm–1) 3382 (m), 3283 (m), 3136, w), 3037 (W), 2977 (w), 2923 (w), 2866 (w), 1732 (m), 1648 (m), 1594 (m).

Crystal data for **1** (form I): $C_{20}H_{21}N_5O_2$, M = 363.42, Colourless Needle, 0.31 × 0.14 × 0.06 mm^3, triclinic, space group *P*-1 (No. 2), a = 5.8615(2), b = 11.0671(4), c = 14.0882(5) Å, α = 91.1250(10), β = 98.7050(10), γ = 97.0080(10)°, V = 895.95(5) Å^3, Z = 2, D_c = 1.347 g/cm^3, F_{000} = 384, Smart 6K, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 61.0º, 16676 reflections collected, 5478 unique (R_{int} = 0.0371). Final *GooF* = 1.026, *R1* = 0.0511, *wR2* = 0.1364, *R* indices based on 3835 reflections with I >2sigma(I) (refinement on F^2), 245 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.091 mm^{-1}.

Crystal data for **1** (form II): $C_{20}H_{21}N_5O_2$, M = 363.42, Colourless Needle, 0.27 × 0.16 × 0.09 mm^3, triclinic, space group *P*-1 (No. 2), a = 4.594(4), b = 7.122(6), c = 28.06(3) Å, α = 93.46(2), β = 92.554(15), γ = 104.922(15)°, V = 883.7(14) Å^3, Z = 2, D_c = 1.370 g/cm^3, F_{000} = 384, Smart-6K, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 50.0º, 1788 reflections collected, 1780 unique (R_{int} = 0.0000). Final *GooF* = 1.071, *R1* = 0.0698, *wR2* = 0.2140, *R* indices based on 1359 reflections with I >2sigma(I) (refinement on F^2), 250 parameters, 69 restraints. Lp and absorption corrections applied, μ = 0.092 mm^{-1}.

Crystal data for [{Cu(μ-κ-*O,O,N,N*-**1**)(MeOH)}$_6$](MeCO$_2$)$_6$·6MeOH: $C_{144}H_{186}Cu_6N_{30}O_{36}$, M = 3294.53, Blue Prism, 0.13 × 0.11 × 0.05 mm^3, trigonal, space group *R*-3 (No. 148), a = b = 31.7325(8), c = 13.6585(7) Å, V = 11910.8(10) Å^3, Z = 3, D_c = 1.378 g/cm^3, F_{000} = 5166, SMart - 6K, MoKα radiation, λ = 0.71073 Å, T =

120(2)K, $2\theta_{max}$ = 50.0º, 22616 reflections collected, 4635 unique (R_{int} = 0.1729). Final *GooF* = 0.811, *R1* = 0.0530, *wR2* = 0.1140, *R* indices based on 1988 reflections with I >2sigma(I) (refinement on F^2), 331 parameters, 3 restraints. Lp and absorption corrections applied, μ = 0.872 mm^{-1}. **Mass Spectrum:** ES^+ *m/z* = 364 [10%] ($C_{20}H_{21}N_5O_2$) + H^+, *m/z* = 386 [38%] ($C_{20}H_{21}N_5O_2$) + Na^+, *m/z* = 457 [100%] ($C_{21}H_{24}CuN_5O_3$) = (Cu + **1**$^-$ + MeOH), *m/z* = 788 [95%] $C_{40}H_{40}CuN_{10}O_4$ + H^+ = (Cu + 2(**1**$^-$) + H^+), *m/z* = 1574 [12%] 6($C_{23}H_{27}CuN_5O_5$) + 2Na^+

Crystal data for *mer*-[Cd(κ-*O,N,N*-**1**)$_2$] ·2MeOH·2H_2O: $C_{42}H_{48}CdN_{10}O_8$, *M* = 933.30, colourless block, 0.11 × 0.07 × 0.04 mm^3, monoclinic, space group $P2_1$ (No. 4), *a* = 12.329(7), *b* = 12.877(7), *c* = 14.883(6) Å, β = 91.625(18)°, *V* = 2362(2) $Å^3$, *Z* = 2, D_c = 1.312 g/cm^3, F_{000} = 964, Smart 6K, MoKα radiation, λ = 0.71073 Å, *T* = 120(2)K, $2\theta_{max}$ = 50.0º, 13397 reflections collected, 8279 unique (R_{int} = 0.0583). Final *GooF* = 1.038, *R1* = 0.0712, *wR2* = 0.1631, *R* indices based on 6016 reflections with I >2sigma(I) (refinement on F^2), 561 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.521 mm^{-1}. Absolute structure parameter = 0.02(5) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Crystal packing energy calculations

Ligand 1 form I

Gavezzotti, A., Acc. Chem. Res. 1994, 27, 309-314
Gavezzotti, A., Filippini, G., J. Phys. Chem., 1994, 98 (18), 4831-4837

Calculated inter-molecular potentials:
mol1 mol2 distance energy (kJ/mol)
0 1 5.8615 -87.9503
0 2 8.93579 -59.8004
0 3 8.08581 -59.6

Hydrogen normalisation: On

Packing Energy:
PE = -161.71 kJ/mol 40 interactions
PE = -165.09 kJ/mol 120 interactions
PE = -165.45 kJ/mol 160 interactions
PE = -165.55 kJ/mol 180 interactions
PE = -165.59 kJ/mol 190 interactions
PE = -165.62 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Unified (UNI) pair-potential parameters:

atom1	code1	atom2	code2	A	B	C
O1	17	O1	17	195309.1	3.74	1335.0
O1	17	N1	23	268571.0	3.86	1523.0
O1	17	C1	3	393086.8	3.74	2682.0
O1	17	H1E	1	295432.3	4.82	439.3
O1	17	N3	19	268571.0	3.86	1523.0
O1	17	H3N	27	15095080.0	7.78	995.8
N1	23	N1	23	365263.0	3.65	2891.0
N1	23	C1	3	491494.0	3.86	2791.0
N1	23	H1E	1	228279.0	4.52	502.1
N1	23	N3	19	365263.2	3.65	2891.0
N1	23	H3N	27	30190070.0	7.78	1992.0
C1	3	C1	3	226145.2	3.47	2418.0
C1	3	H1E	1	120792.1	4.10	472.8
C1	3	N3	19	491494.0	3.86	2791.0
C1	3	H3N	27	120792.1	4.10	472.8
H1E	1	H1E	1	24158.0	4.01	109.2

H1E	1	N3	19	228279.0	4.52	502.1
H1E	1	H3N	27	24158.0	4.01	109.2
N3	19	N3	19	365263.2	3.65	2891.0
N3	19	H3N	27	228279.0	4.52	502.1
H3N	27	H3N	27	24158.0	4.01	109.2

Ligand 1 form II

Notes:
close contact of 1.98265 found between O1 and H3N
close contact of 1.86915 found between O1 and H4N
close contact of 1.74834 found between H19 and H1B

Calculated inter-molecular potentials:
mol1 mol2 distance energy (kJ/mol)
0 1 4.5914 -131.358
0 2 7.40409 -31.4151
0 3 7.115 -24.7166

Hydrogen normalisation: On

Packing Energy:
PE = -238.64 kJ/mol 40 interactions
PE = -243.23 kJ/mol 120 interactions
PE = -243.58 kJ/mol 160 interactions
PE = -243.67 kJ/mol 180 interactions
PE = -243.71 kJ/mol 190 interactions
PE = -243.74 kJ/mol 200 interactions

Potential = A*exp(-Br) - Cr(-6)

Unified (UNI) pair-potential parameters:
atom1 code1 atom2 code2 A B C
O1 17 O1 17 195309.1 3.74 1335.0
O1 17 N1 23 268571.0 3.86 1523.0
O1 17 C1 3 393086.8 3.74 2682.0
O1 17 H1B 1 295432.3 4.82 439.3
O1 17 N3 19 268571.0 3.86 1523.0
O1 17 H3N 27 15095080.0 7.78 995.8
N1 23 N1 23 365263.0 3.65 2891.0
N1 23 C1 3 491494.0 3.86 2791.0
N1 23 H1B 1 228279.0 4.52 502.1
N1 23 N3 19 365263.2 3.65 2891.0
N1 23 H3N 27 30190070.0 7.78 1992.0
C1 3 C1 3 226145.2 3.47 2418.0
C1 3 H1B 1 120792.1 4.10 472.8
C1 3 N3 19 491494.0 3.86 2791.0
C1 3 H3N 27 120792.1 4.10 472.8
H1B 1 H1B 1 24158.0 4.01 109.2
H1B 1 N3 19 228279.0 4.52 502.1
H1B 1 H3N 27 24158.0 4.01 109.2
N3 19 N3 19 365263.2 3.65 2891.0
N3 19 H3N 27 228279.0 4.52 502.1
H3N 27 H3N 27 24158.0 4.01 109.2