Electronic Supplementary Material (ESI) for Dalton Transactions

Supramolecular isomerism and solvatomorphism in a novel coordination compound

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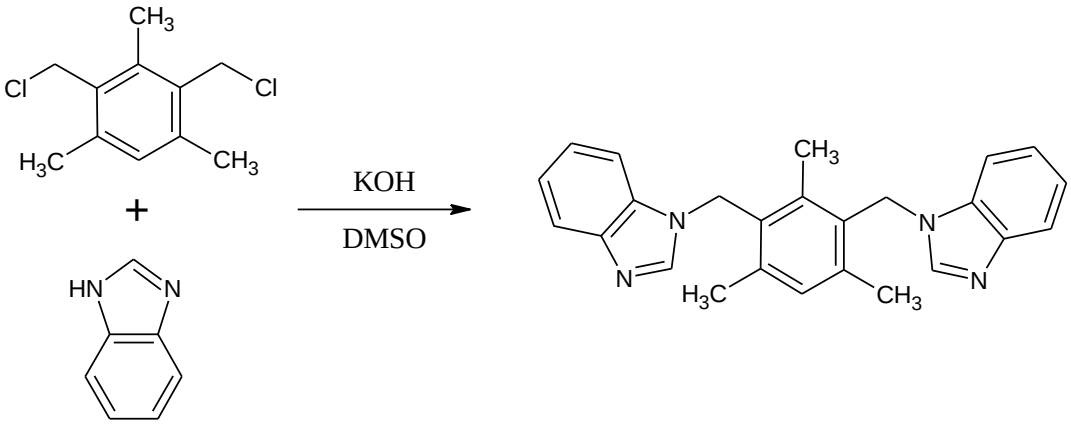
Supplementary Information

SYNTHESIS OF THE LIGAND (L)

The synthetic method used is a modification of a method previously described in literature.[1]

1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (L)



Benzimidazol (6.60 mmol, 0.780 g) and potassium hydroxide (25 mmol, 1.403 g) were placed in suspension in 15 ml dimethylsulfoxide. The mixture was stirred at room temperature for 1.5 hours after which 2,4-bis-(chloromethyl)-1,3,5-tri-methylbenzene (3 mmol, 0.651 g) was added. After stirring for another four hours, 40 ml water was added to the milky white mixture to precipitate a white solid. The product was extracted by washing the water/DMSO mixture with dichloromethane (4 x 20 ml). The DCM solution was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield a drop of light brown liquid. An excess of diethyl ether was added to the liquid to yield light brown microcrystals. The product was filtered and washed with ethyl acetate to yield 0.851 g cream-coloured solid particles.

Melting point: 242.5 °C **Yield: 74.3 %**

δ_H (600 MHz, DMSO-d_6)

δ 2.12 (s, 3 H) 2.28 (s, 6 H) 5.44 (s, 4 H) 7.12 (s, 1 H) 7.17 - 7.23 (m, 4 H) 7.42 - 7.47 (m, 2 H) 7.63 - 7.68 (m, 2 H) 7.76 (s, 2 H)

δ_C (300 MHz, DMSO-d_6)

15.44, 19.68, 43.34, 110.48, 119.56, 121.72, 122.48, 130.12, 131.03, 134.04, 138.15, 138.24, 142.84, 143.42.

POWDER X-RAY DIFFRACTION (PXRD)

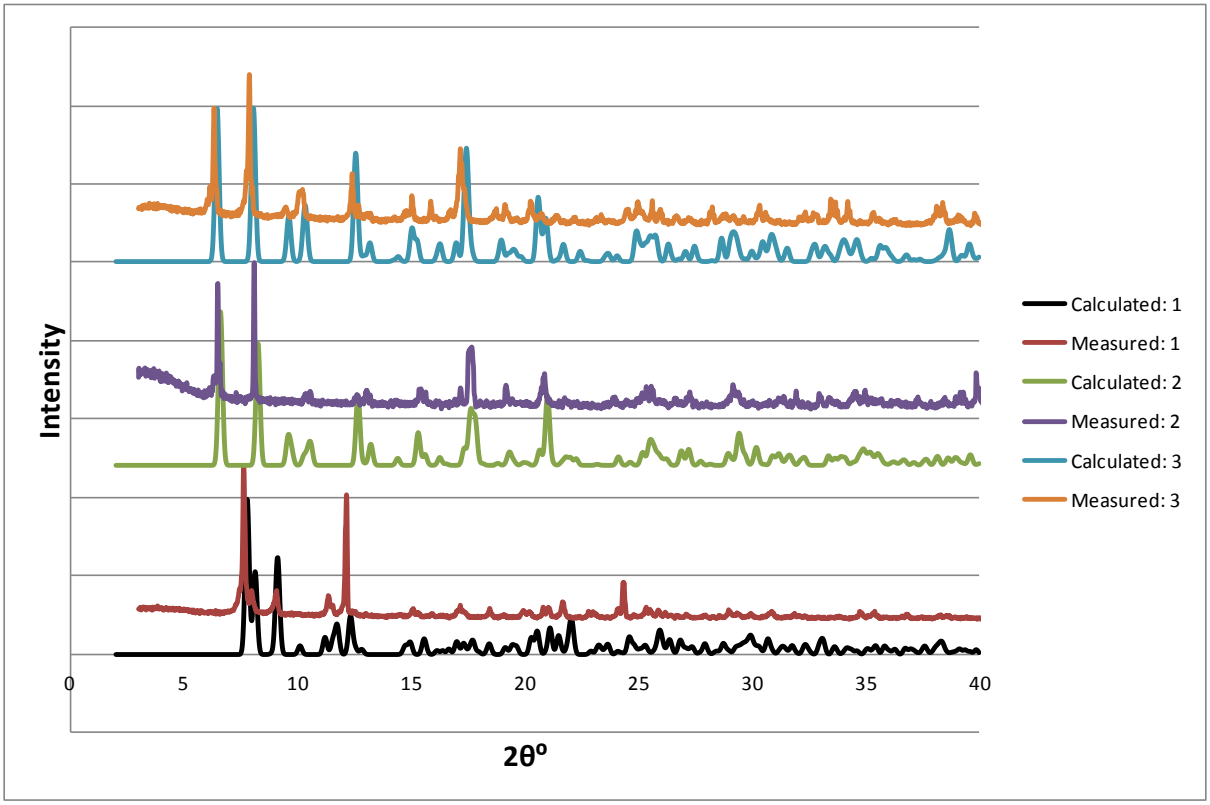


Figure 1 The calculated powder patterns for compounds **1**, **2** and **3** are shown in black, green and blue, respectively and the experimental powder patterns for the compounds are shown in red, purple and orange, respectively. Note that the powder patterns for compounds **2** and **3** are very similar, owing to their isostructurality.

THERMOGRAVIMETRIC ANALYSIS (TGA)

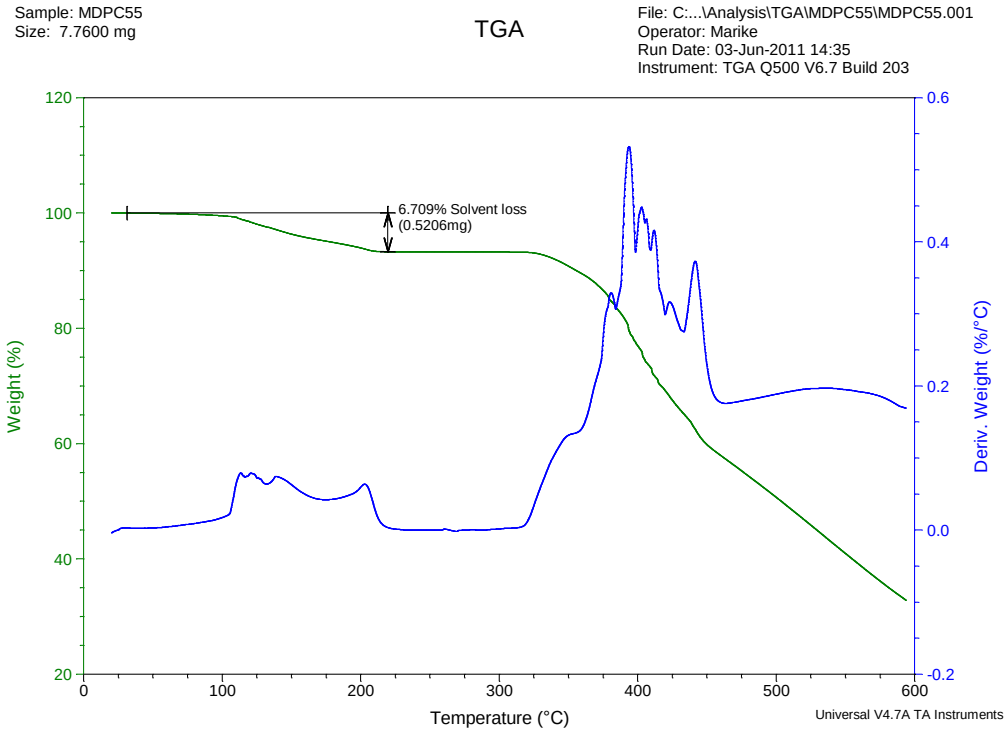


Figure 2 TGA result for compound **1**. The 6.7 % solvent loss correlates well with the calculated amount of 5.9 %.

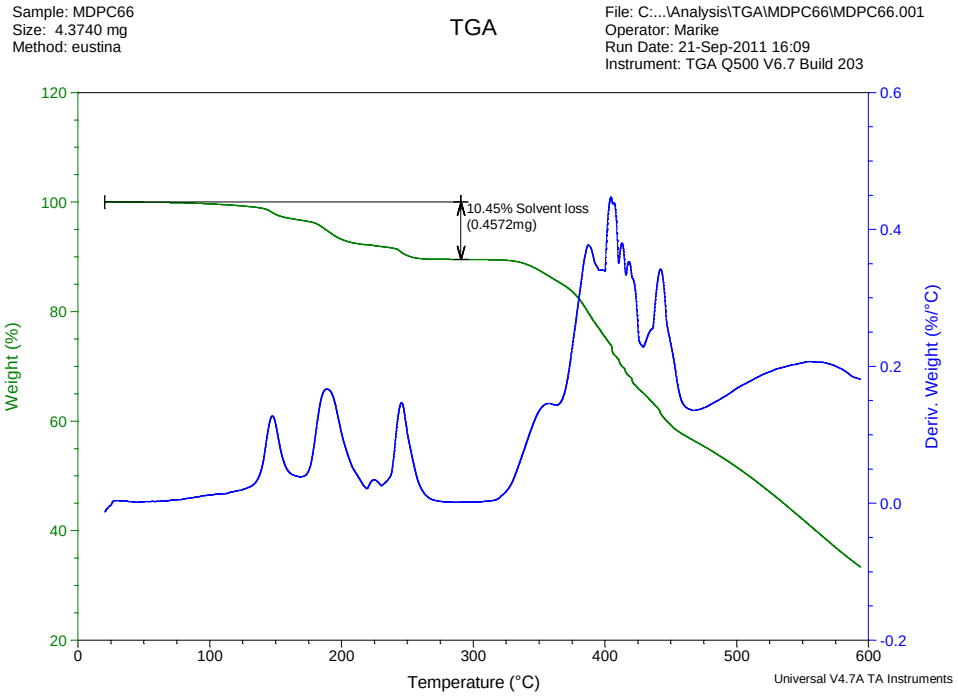


Figure 3 TGA result for compound **1**. The 10.5 % solvent loss correlates well with the calculated amount of 10.0 %.

CRYSTAL GROWTH

Colourless plate-shaped crystals of compound **1** were grown by means of layering. 0.03 mmol (10.3 mg) of $CdBr_2$ were dissolved in 2 ml methanol. This solution was layered onto a solution of **L** (0.03 mmol, 11.4 mg) in 2 ml dichloromethane with a 2 ml methanol buffer layer.

The same method of layering was used to obtain colourless block-shaped crystals of compound **2**. Dimethylformamide was used instead of dichloromethane, and acetonitrile instead of methanol.

Compound **3** was crystallised by dissolving the ligand (0.03 mmol, 11.4 mg) and the metal salt (0.03 mmol, 10.3 mg) in 1 ml DMF each. The solutions were mixed and 2 ml acetone was layered onto the mixture. Colourless block-shaped crystals grew within several days.

X-ray Crystallography

Crystal Information Files – the CheckCIF report for Compound **1** shows a number of A-Alerts. These are due to the fact that the structure was refined as a twin.

Non-merohedral twin. First twin component: 70 %, second twin component: 30 %.

Transformation between the two components: [1 0 0], [0.905 -1 0], [0.883 0 -1]

CRYSTALLOGRAPHIC TABLES

Table 1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{26}H_{26}Br_2CdCl_2N_4$	
Formula weight	737.63	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions (Å, °)	a = 10.8233(16)	α = 82.755(2)
	b = 15.163(2)	β = 74.833(2)
	c = 18.137(3)	γ = 71.208(2)
Volume (Å^3)	2716.8(7)	
Z	4	
Calculated density (g cm^{-3})	1.803	
Absorption coefficient (mm^{-1})	3.965	
F_{000}	1448	
Crystal size (mm^3)	0.36 × 0.25 × 0.09	
θ range for data collection (°)	1.88 to 27.66	
Miller index ranges	$-14 \le h \le 13$, $-19 \le k \le 19$, $-23 \le l \le 23$	
Reflections collected	24450	
Independent reflections	12541 [R_{int} = 0.0871]	
Completeness to θ_{max} (%)	98.7	
Max. and min. transmission	0.7167 and 0.3294	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12541 / 0 / 637	
Goodness-of-fit on F^2	0.995	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0683, $wR2$ = 0.1721	
R indices (all data)	$R1$ = 0.0933, $wR2$ = 0.1823	
Largest diff. peak and hole (e Å^{-3})	3.422 and -2.501	

Table 2. Crystal data and structure refinement for compound **2**.

Empirical formula	$C_{27}H_{27}Br_2CdN_5$	
Formula weight	693.76	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	*P*2/*n*	
Unit cell dimensions (Å, °)	*a* = 14.7707(16)	α = 90.00
	b = 10.7210(12)	β = 111.3540(10)
	c = 18.482(2)	γ = 90.00
Volume (Å^3)	2725.8(5)	
Z	4	
Calculated density (g cm^{-3})	1.691	
Absorption coefficient (mm^{-1})	3.757	
F_{000}	1368	
Crystal size (mm^3)	0.39 × 0.21 × 0.11	
θ range for data collection (°)	2.21 to 28.82	
Miller index ranges	$-19 \le h \le 17$, $-12 \le k \le 13$, $-21 \le l \le 24$	
Reflections collected	17139	
Independent reflections	6433 [R_{int} = 0.0156]	
Completeness to θ_{max} (%)	90.2	
Max. and min. transmission	0.6827 and 0.3220	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6433 / 0 / 320	
Goodness-of-fit on F^2	1.025	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0182, *wR*2 = 0.0445	
R indices (all data)	*R*1 = 0.0209, *wR*2 = 0.0454	
Largest diff. peak and hole (e Å^{-3})	0.666 and -0.292	

Table 3. Crystal data and structure refinement for compound **3**.

Empirical formula	$C_{28}H_{31}Br_2CdN_5O$	
Formula weight	725.80	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	*P*2/*n*	
Unit cell dimensions (Å, °)	*a* = 15.1378(11)	α = 90.00
	b = 10.9825(8)	β = 112.6550(10)
	c = 18.4356(13)	γ = 90.00
Volume (Å^3)	2828.4(4)	
Z	4	
Calculated density (g cm^{-3})	1.704	
Absorption coefficient (mm^{-1})	3.628	
F_{000}	1440	
Crystal size (mm^3)	0.39 × 0.17 × 0.11	
θ range for data collection (°)	1.85 to 28.80	
Miller index ranges	$-20 \le h \le 20$, $-14 \le k \le 10$, $-24 \le l \le 24$	
Reflections collected	17862	
Independent reflections	6823 [R_{int} = 0.0150]	
Completeness to θ_{max} (%)	92.4	
Max. and min. transmission	0.6910 and 0.3320	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6823 / 0 / 339	
Goodness-of-fit on F^2	1.037	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0171, *wR*2 = 0.0411	
R indices (all data)	*R*1 = 0.0199, *wR*2 = 0.0419	
Largest diff. peak and hole (e Å^{-3})	0.396 and -0.306	

REFERENCES

1. Mukherjee, P. S.; Ghosh, S.; Chakrabarty, R., Coordination driven self-assembly of four new molecular boats using a flexible imidazole-containing donor linker. *Dalton T* 2008, (14), 1850-1856.