Supplementary Material (ESI) for Chemical Communications

Experimental details

Synthesis of Cu(1,1,3,6,6,8-Hexamethyl-decahydro-3a,5a,8a,10a-tetra-azapyrene)Cl_2

(Cu**2**Cl_2): 0.170 g (0.001 mol) $CuCl_2 \cdot 2H_2O$ in 10ml of MeOH was added to 0.31g (0.001 mol) of **2** (tetA synthesized according to a literature procedure; R. W. Hay and G. A. Lawrence. *J. Chem. Soc., Perkin 1* 1975, 591.) in 20ml of MeOH with stirring. The solution was then heated at reflux for 16 hours. During the reaction, the solution's colour changed from the initial dark green color to pale red and finally to a yellow-green upon cooling. This reaction yielded light green, needle-like crystals upon cooling. Yield: 0.278 g (63%).

Anal. Cald for $CuC_{18}H_{34}N_4Cl_2 \cdot 0.5\ H_2O$: C, 48.05; H, 7.84; N, 12.45. Found: C, 48.04; H, 7.64; N, 12.33. λ_{max}/nm, (ε/ $M^{-1}cm^{-1}$); 285(2400), 389(900). FAB^+ mass spectrum (NBA), m/z = 442 (Cu**2**Cl_2^+).

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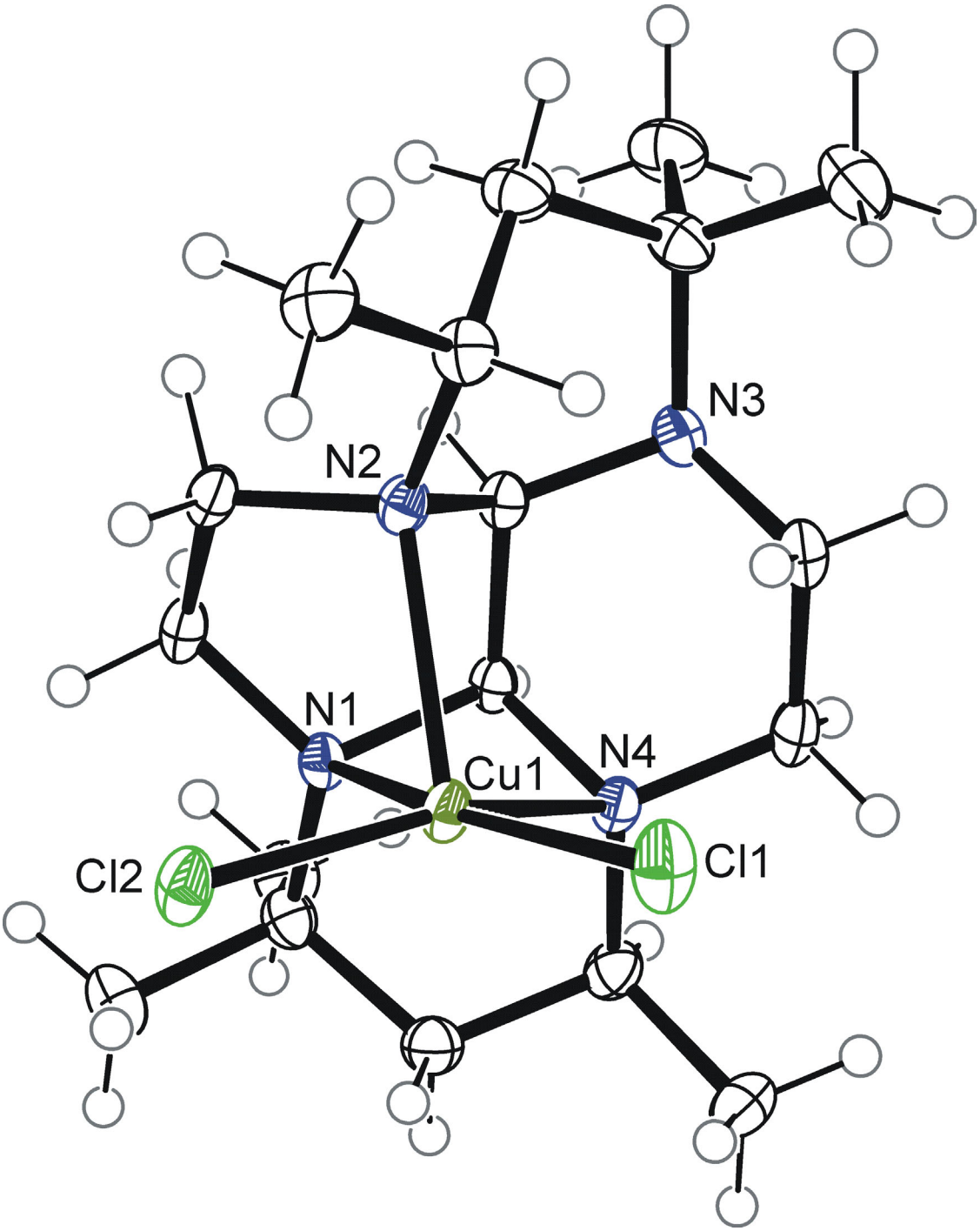
Crystallographic details for Cu**2**Cl_2



ORTEP (50% probability ellipsoids)

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Table 1. Crystal data and structure refinement for $Cu\mathbf{2}Cl_2$.

Identification code	sja68	
Empirical formula	C18 H34 Cl2 Cu N4	
Formula weight	440.93	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 8.5250(8) Å	α= 90°.
	b = 18.9082(17) Å	β= 97.997(8)°.
	c = 12.7881(13) Å	γ = 90°.
Volume	2041.3(3) $Å^3$	
Z	4	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	1.341 mm^{-1}	
F(000)	932	
Crystal size	0.25 x 0.3 x 0.3 mm^3	
Theta range for data collection	2.64 to 34.72°.	
Index ranges	-13<=h<=13, -29<=k<=30, -20<=l<=18	
Reflections collected	45368	
Independent reflections	8731 [R(int) = 0.0703]	
Completeness to theta = 34.72°	99.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8731 / 0 / 261	
Goodness-of-fit on F^2	0.853	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0792	
R indices (all data)	R1 = 0.0640, wR2 = 0.0856	
Extinction coefficient	0.0066(5)	
Largest diff. peak and hole	0.607 and -0.897 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sja68. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	3484(1)	2947(1)	3758(1)	29(1)
Cl(2)	6501(1)	2361(1)	2485(1)	25(1)
N(1)	8172(1)	2093(1)	4958(1)	17(1)
N(2)	7758(1)	3415(1)	4717(1)	17(1)
N(3)	7067(1)	3641(1)	6497(1)	19(1)
N(4)	5919(1)	2287(1)	5716(1)	17(1)
C(1)	7650(1)	2429(1)	5910(1)	16(1)
C(2)	7991(2)	3224(1)	5868(1)	17(1)
C(3)	9623(2)	2432(1)	4679(1)	20(1)
C(4)	9222(2)	3189(1)	4307(1)	20(1)
C(5)	7392(2)	4183(1)	4583(1)	22(1)
C(6)	8269(2)	4597(1)	5516(1)	26(1)
C(7)	7629(2)	4395(1)	6554(1)	24(1)
C(8)	5362(2)	3499(1)	6280(1)	22(1)
C(9)	5064(2)	2720(1)	6416(1)	22(1)
C(10)	5670(2)	1512(1)	5906(1)	22(1)
C(11)	6510(2)	1078(1)	5142(1)	23(1)
C(12)	8219(2)	1300(1)	5056(1)	21(1)
C(13)	7700(2)	4454(1)	3506(1)	28(1)
C(14)	8937(2)	4450(1)	7500(1)	31(1)
C(15)	6290(2)	4902(1)	6722(2)	34(1)
C(16)	3911(2)	1322(1)	5762(2)	31(1)
C(17)	8681(2)	971(1)	4043(2)	29(1)
C(18)	9382(2)	1047(1)	6007(1)	27(1)
Cu(1)	5970(1)	2529(1)	4132(1)	17(1)

Table 3. Bond lengths [Å] and angles [°] for sja68.

Cl(1)-Cu(1)	2.2506(4)	C(3)-N(1)-C(12)	115.94(11)
Cl(2)-Cu(1)	2.2374(5)	C(1)-N(1)-C(12)	111.29(11)
N(1)-C(3)	1.4796(17)	C(3)-N(1)-Cu(1)	114.29(9)
N(1)-C(1)	1.4955(17)	C(1)-N(1)-Cu(1)	84.27(7)
N(1)-C(12)	1.5053(19)	C(12)-N(1)-Cu(1)	115.33(9)
N(1)-Cu(1)	2.1833(12)	C(4)-N(2)-C(5)	114.41(11)
N(2)-C(4)	1.4822(17)	C(4)-N(2)-C(2)	105.92(11)
N(2)-C(5)	1.491(2)	C(5)-N(2)-C(2)	110.07(11)
N(2)-C(2)	1.5018(18)	C(4)-N(2)-Cu(1)	103.06(9)
N(2)-Cu(1)	2.3170(12)	C(5)-N(2)-Cu(1)	123.35(9)
N(3)-C(2)	1.4379(18)	C(2)-N(2)-Cu(1)	97.72(8)
N(3)-C(8)	1.4658(19)	C(2)-N(3)-C(8)	113.56(12)
N(3)-C(7)	1.502(2)	C(2)-N(3)-C(7)	110.54(11)
N(4)-C(9)	1.4771(18)	C(8)-N(3)-C(7)	118.98(12)
N(4)-C(1)	1.4866(17)	C(9)-N(4)-C(1)	111.15(11)
N(4)-C(10)	1.505(2)	C(9)-N(4)-C(10)	110.40(11)
N(4)-Cu(1)	2.0831(13)	C(1)-N(4)-C(10)	107.91(11)
C(1)-C(2)	1.533(2)	C(9)-N(4)-Cu(1)	123.13(10)
C(3)-C(4)	1.533(2)	C(1)-N(4)-Cu(1)	88.17(8)
C(5)-C(13)	1.526(2)	C(10)-N(4)-Cu(1)	113.17(9)
C(5)-C(6)	1.531(2)	N(4)-C(1)-N(1)	100.86(10)
C(6)-C(7)	1.552(2)	N(4)-C(1)-C(2)	111.08(11)
C(7)-C(15)	1.528(2)	N(1)-C(1)-C(2)	107.95(11)
C(7)-C(14)	1.531(2)	N(3)-C(2)-N(2)	114.14(11)
C(8)-C(9)	1.509(2)	N(3)-C(2)-C(1)	113.33(11)
C(10)-C(16)	1.528(2)	N(2)-C(2)-C(1)	105.67(11)
C(10)-C(11)	1.529(2)	N(1)-C(3)-C(4)	108.73(10)
C(11)-C(12)	1.535(2)	N(2)-C(4)-C(3)	108.77(11)
C(12)-C(18)	1.534(2)	N(2)-C(5)-C(13)	111.70(13)
C(12)-C(17)	1.537(2)	N(2)-C(5)-C(6)	109.68(12)
		C(13)-C(5)-C(6)	113.93(13)
		C(5)-C(6)-C(7)	110.41(13)
		N(3)-C(7)-C(15)	111.23(13)
		N(3)-C(7)-C(14)	107.18(13)
		C(15)-C(7)-C(14)	108.82(15)
C(3)-N(1)-C(1)	111.47(11)	N(3)-C(7)-C(6)	109.91(12)

C(15)-C(7)-C(6)	108.88(14)	C(11)-C(12)-C(17)	107.86(13)
C(14)-C(7)-C(6)	110.82(14)	N(4)-Cu(1)-N(1)	65.15(4)
N(3)-C(8)-C(9)	109.60(12)	N(4)-Cu(1)-Cl(2)	156.72(4)
N(4)-C(9)-C(8)	111.45(12)	N(1)-Cu(1)-Cl(2)	97.40(3)
N(4)-C(10)-C(16)	111.59(13)	N(4)-Cu(1)-Cl(1)	97.88(3)
N(4)-C(10)-C(11)	109.28(12)	N(1)-Cu(1)-Cl(1)	163.03(3)
C(16)-C(10)-C(11)	109.59(13)	Cl(2)-Cu(1)-Cl(1)	99.067(17)
C(10)-C(11)-C(12)	115.64(13)	N(4)-Cu(1)-N(2)	86.94(5)
N(1)-C(12)-C(18)	112.54(13)	N(1)-Cu(1)-N(2)	68.55(4)
N(1)-C(12)-C(11)	105.27(11)	Cl(2)-Cu(1)-N(2)	101.33(3)
C(18)-C(12)-C(11)	111.93(13)	Cl(1)-Cu(1)-N(2)	111.87(3)
N(1)-C(12)-C(17)	109.90(13)		
C(18)-C(12)-C(17)	109.19(13)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for sja68. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	19(1)	48(1)	19(1)	-1(1)	0(1)	8(1)
Cl(2)	19(1)	42(1)	13(1)	-1(1)	3(1)	-2(1)
N(1)	17(1)	20(1)	15(1)	-1(1)	4(1)	1(1)
N(2)	17(1)	21(1)	14(1)	2(1)	3(1)	0(1)
N(3)	21(1)	21(1)	16(1)	-1(1)	4(1)	2(1)
N(4)	15(1)	22(1)	16(1)	0(1)	3(1)	0(1)
C(1)	15(1)	22(1)	11(1)	0(1)	2(1)	1(1)
C(2)	15(1)	21(1)	14(1)	1(1)	2(1)	1(1)
C(3)	14(1)	30(1)	18(1)	1(1)	5(1)	1(1)
C(4)	16(1)	26(1)	17(1)	0(1)	5(1)	-2(1)
C(5)	24(1)	23(1)	18(1)	4(1)	2(1)	1(1)
C(6)	33(1)	21(1)	22(1)	1(1)	4(1)	-3(1)
C(7)	31(1)	21(1)	20(1)	-2(1)	3(1)	1(1)
C(8)	20(1)	27(1)	19(1)	-2(1)	6(1)	4(1)
C(9)	19(1)	30(1)	19(1)	0(1)	8(1)	1(1)
C(10)	22(1)	24(1)	19(1)	3(1)	5(1)	-3(1)
C(11)	25(1)	22(1)	23(1)	-1(1)	4(1)	-2(1)
C(12)	23(1)	21(1)	20(1)	1(1)	4(1)	3(1)
C(13)	34(1)	29(1)	20(1)	7(1)	3(1)	-1(1)
C(14)	39(1)	31(1)	22(1)	-5(1)	-2(1)	-6(1)
C(15)	45(1)	26(1)	32(1)	-4(1)	10(1)	7(1)
C(16)	25(1)	34(1)	35(1)	-1(1)	9(1)	-9(1)
C(17)	34(1)	27(1)	27(1)	-5(1)	8(1)	7(1)
C(18)	29(1)	27(1)	26(1)	6(1)	2(1)	7(1)
Cu(1)	14(1)	25(1)	12(1)	1(1)	2(1)	0(1)

Computational details

Table 5. Comparison of observed (solid state, 150K) and calculated bond lengths [Å] for Cu**1**Cl_2 and Cu**2**Cl_2. (The bond lengths for Cu**1**Cl_2 are taken from T. J. Hubin, N. W. Alcock, L. L. Seib and D. H. Busch, *Inorg. Chem.*, 2002, **41**, 7006.)

	Observed	Calculated
Cu**1**Cl_2		
Cu-Cl(1)	2.222	2.269
Cu-Cl(2)	2.228	2.272
Cu-N(1)	2.118	2.196
Cu-N(2)	2.120	2.204
Cu**2**Cl_2		
Cu-Cl(1)	2.251	2.267
Cu-Cl(2)	2.237	2.258
Cu-N(1)	2.183	2.203
Cu-N(2)	2.317	2.400
Cu-N(4)	2.083	2.198

Energy analysis:

The bonding has been analysed by decomposing the molecular bonding or atomization energy (E_B) is as,

$$E_B = E_O + E_P + E_E$$

where E_O, E_P and E_E represent orbital mixing, Pauli repulsion and electrostatic interaction terms respectively. Descriptions of the physical significance of these properties have been given by Landrum, Goldberg and Hoffmann[1i] and Baerends and co-workers[1,2]. Both E_O and E_P arise from orbital interaction effects with the former stabilizing and the latter destabilizing. E_O represents the effect of charge transfer, orbital mixing and polarization when filled and empty atomic orbitals overlap.

Cyclam + $CuCl_2$ --> complex

For **1** (all chair), ΔE = -311 $kJmol^{-1}$.
For **1** (two twist boat), ΔE = -298 $kJmol^{-1}$.
For **2** (all chair), ΔE = -287 $kJmol^{-1}$
For **2** (two twist boat), ΔE = -306 $kJmol^{-1}$

Geometry optimizations and energy analyses were performed at the unrestricted UBP86/TZP level with ZORA relativistic effects and frozen (n-1) cores using ADF 2002.02.[2,3,4] Relative energies were also determined at the unrestricted UB3LYP/LanL2DZ level using Gaussian 98.[5]

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