Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 260–262

Molecular tectonics: from a binuclear metallamacrocycle to a 1D isostructural coordination network based on tetracyanomethyl[1.1.1.1]metacyclophane and a silver cation

Ekaterina F. Chernova, Alexander S. Ovsyannikov, Sylvie Ferlay, Svetlana E. Solovieva, Igor S. Antipin, Alexander I. Konovalov, Nathalie Kyritsakas and Mir Wais Hosseini

The synthesis of 4,11,18,25-tetrakis(chloromethyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodeca-methyl[1.1.1.1]metacyclophane **1** was achieved by modifying the previously reported procedure,[1] using $CHCl_3$ instead of CS_2.

Elemental analyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

FT-IR spectra were recorded on a Perkin Elmer spectrometer.

Data for X-Ray analysis were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ= 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97.[2] The hydrogen atoms were introduced at calculated positions and not refined (riding model). They can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1504654-1504656.

Synthesis of 4,11,18,25-tetracyanomethyl-3,5,7,10,12,14,17,19,21,24,26,28-dodeca-methyl[1.1.1.1]metacyclophane 2

1g (1.38 mmol) of **1** was suspended in a DMF/acetone 3:1 mixture (40 ml). 0.72 g of KCN (720 mg, 11.06 mmol) was added. The reaction mixture was stirred 30 h upon reflux. After cooling to room temperature, the solvent was evaporated under reduced temperature and the residue was treated with 50 ml of CH_2Cl_2. After filtration, the organic solvent was evaporated to dryness. After addition of 50

1 S. Pappalardo, G. Ferguson and J. F. Gallagher, *J. Org. Chem.*, 1992, **57**, 7102.
2 G. M. Sheldrick, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.

ml of MeOH to the residue and filtration, the pure compound **2** was obtained as a white powder (0.77g, yield 81%).

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ (ppm) 1.07 (s, 12H, *para*-C*H*$_3$), 2.43 (s, 24H, *ortho*-C*H*$_3$), 3.73 (s, 8H, -C*H*$_2$-CN), 4.02 (s, 8H, Ar-C*H*$_2$-Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C) δ: 17.8, 18.9, 20.1, 33.3, 118.3, 126.1, 132.4, 135.8, 138.2. IR, ν (C ≡N) 2246 cm^{-1}. Mp: 246 °C, MALDI TOF: m/z = 684.24 [M^+] (calculated 684.96). Elemental Analysis for $C_{48}H_{52}N_4$, %, found: C, 84.02; H, 7.62; N, 8.15; calc.: C, 84.17; H, 7.65; N, 8.18.

Crystallisation conditions

$[Ag_3(C_{48}H_{52}N_4)_3(BF_4)_3]$ **2**-$AgBF_4$: In a crystallization tube (diameter 4 mm), a solution of **2** (5 mg, 7.3 x 10^{-3} mmol) in $CHCl_3$ (1 ml) was layered with a $CHCl_3$/MeOH (1/1) mixture (0.5 ml). A solution of $AgBF_4$ (3.39 mg, 14.6 x 10^{-3} mmol) in MeOH (1 ml) was then carefully added. At room temperature, slow diffusion in the dark afforded colourless crystals suitable for X-ray diffraction after several days. Elemental Analysis for $C_{144}H_{156}Ag_3B_3F_{12}N_{12}$, % found: C, 65.76; H, 5.81; N, 6.25; calc.: C, 65.54; H, 5.96; N, 6.37.

$[Ag_3(C_{48}H_{52}N_4)_3(NO_3)_3]$ **2**-$AgNO_3$: In a crystallization tube (diameter 4 mm), a solution of **2** (5 mg, 7.3 x 10^{-3} mmol) in $CHCl_3$ (1 ml) was layered with a $CHCl_3$/MeOH (1/1) mixture (0.5 ml). A solution of $AgNO_3$ (2.48 mg, 14.6 x 10^{-3} mmol) in MeOH (1 ml) was then carefully added. Slow diffusion in the dark and at room temperature afforded colourless crystals suitable for X-ray diffraction after several days. Elemental Analysis for $C_{144}H_{156}Ag_3N_{15}O_9$: % found: C, 67.68; H, 6.05; N, 8.12; calc.: C, 67.44; H, 6.13; N, 8.19.

$[Ag_2(C_{48}H_{52}N_4)_2(NO_3)_2,6(CHCl_3)]$ [(**2**)$_2$-$(AgNO_3)_2$]: In a crystallization tube (diameter 4 mm), a solution of **2** (5 mg, 7.3 x 10^{-3} mmol) in $CHCl_3$ (1 ml) was layered with a $CHCl_3$/MeOH (1/1) mixture (0.5 ml). A solution of $AgNO_3$ (4.96 mg, 29.2 x 10^{-3} mmol) in MeOH (1 ml) was then carefully added. At room temperature, slow diffusion in the dark produced colourless crystals suitable for X-ray diffraction after several days. Elemental Analysis for $C_{102}H_{110}Ag_2Cl_{18}N_{10}O_6$: % found: C, 50.86; H, 4.42; N, 5.56; calc.: C, 50.50; H, 4.57; N, 5.77.

Table S1 Crystal data for [(**2**)$_2$-($AgNO_3$)$_2$].

Empirical formula	{2($C_{48}H_{52}AgN_4$)2(NO_3) 6($CHCl_3$)}	
Formula weight	2425.83	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.7017(9) Å	□□= 73.798(3)°.
	b = 14.8810(9) Å	□□= 69.159(3)°.
	c = 15.5594(10) Å	□ = 86.320(4)°.
Volume	2637.3 (3) Å^3	
Z	1	
Density (calculated)	1.527 Mg/m^3	
Absorption coefficient	0.886 mm^{-1}	
F(000)	1240	
Crystal size	0.050 x 0.0560 x 0.060 mm^3	
Theta range for data collection	1.46 to 30.35°.	
Index ranges	-17<=h<=17, -18<=k<=20, -21<=l<=21	
Reflections collected	78535	
Independent reflections	14260 [R(int) = 0.0721]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9610 and 0.9410	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14260 / 0 / 634	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0706, wR2 = 0.2030	
R indices (all data)	R1 = 0.1221, wR2 = 0.2340	
Largest diff. peak and hole	2.351 and -1.499 e.Å^{-3}	

Table S2 Crystal data for **2**-$AgNO_3$.

Empirical formula	{3($C_{48}H_{52}AgN_4$) 3(NO_3)}	
Formula weight	2564.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	cubic	
Space group	I a -3 d	
Unit cell dimensions	a = 29.2699(9) Å	□□= 90°.
	b = 29.2699(9) Å	□□= 90°.
	c = 29.2699(9) Å	□ = 90°.
Volume	25076(2)Å^3	
Z	8	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	0.530 mm^{-1}	
F(000)	10704	
Crystal size	0.070 x 0.070 x 0.080 mm^3	
Theta range for data collection	1.70 to 30.02°.	
Index ranges	-24<=h<=39, -41<=k<=20, -40<=l<=38	
Reflections collected	3064	
Independent reflections	3064 [R(int) = 0.0616]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9700 and 0.9560	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3064 / 3 / 137	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0885, wR2 = 0.2272	
R indices (all data)	R1 = 0.1526, wR2 = 0.2565	
Largest diff. peak and hole	1.111 and -0.639 e.Å^{-3}	

Table S3 Crystal data for **2**-$AgBF_4$.

Empirical formula	{3($C_{48}H_{52}AgN_4$) 3(BF_4)}	
Formula weight	2638.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	cubic	
Space group	I a -3 d	
Unit cell dimensions	a = 29.4672(11) Å	□□= 90°.
	b = 29.4672(11) Å	□□= 90°.
	c = 29.4672(11) Å	□ = 90°.
Volume	25587.(3) $Å^3$	
Z	8	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	0.529 mm^{-1}	
F(000)	10944	
Crystal size	0.050 x 0.050 x 0.060 mm^3	
Theta range for data collection	1.69 to 30.03°.	
Index ranges	-36<=h<=21, -26<=k<=27, -16<=l<=41	
Reflections collected	24812	
Independent reflections	3125 [R(int) = 0.0567]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9800 and 0.9610	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3125 / 2 / 129	
Goodness-of-fit on F^2	1.192	
Final R indices [I>2sigma(I)]	R1 = 0.1043, wR2 = 0.3306	
R indices (all data)	R1 = 0.1752, wR2 = 0.3734	
Largest diff. peak and hole	1.318 and -0.899 e.$Å^{-3}$	