Supplementary data

Novel 36-membered dodecanuclear manganese
metalladiazamacrocycle

Rohith P. John, Kyungjae Lee and Myoung Soo Lah[*]

Department of Chemistry and Applied Chemistry, College of Science and Technology,
Hanyang University, Ansan, Kyunggi-do 426-791, Korea, E-mail:
mslah@hanyang.ac.kr

Contents:

Synthesis of ligand N-*trans*-2-pentenoylsalicyclichydrazide (1): To a 20mL of chloroform solution at 0°C, containing 1.544 mL (11mmol) of triethylamine and 1.032gm (10mmol) of *trans*-2-pentenoic acid was added a 1.244 mL (10 mmol) of trimethylacetyl chloride with stirring. The solution is then brought slowly to room temperature. After stirring for 20 minutes 1.398 gm (9 mmol) of salicylic hydrazide was added to it and continued stirring for another 30 minutes. It is then layered with 10ml of hexane; a white suspension appears which is then left aside for complete precipitation. The product obtained was filtered, washed successively with a 1:1 mixture of chloroform and hexane, and then with ether. The compound was recrystallised from ethanol to yield 1.502 gm (71%). Anal. Calc for $C_{12}H_{14}N_2O_3$: C 61.53, H 6.02, N 11.96 %, Found C 61.85, H 6.54, N 11.76 %; ESI mass spectrum: m/z 235.1 $(M+1)^+$; ^1H NMR spectrum (300 MHz, DMSO-d^6, ppm, Hz): 11.89 (s (br), 1H, NH), 10.70 (s (br), 1H, NH), 10.40 (s, 1H, OH), 7.91 (d, 1H, J = 7.8), 7.44 (t, 1H, J = 7.8), 6.96 (d, 1H, J = 8.0), 6.94 (t, 1H, J = 7.8), 6.84 (td, 1H, J = 15.6), 6.05 (d, 1H, J = 15.6), 2.20 (q, 2H, CH_2, J = 7.2), 1.02 (t, 3H, CH_3,

J = 7.2), ^{13}C NMR spectrum (75.42 MHz, DMSO-d^6, ppm) 166.20, 163.52 (C=O),

158.82, 146.36, 134.07, 128.62, 120.65, 119.16, 117.32, 114.82, 24.65, 12.39; IR

spectrum (KBr, cm^{-1}): 3172, 3118, 3067, 1673, 1646 ($\nu_{C=N}$ stretching), 1559, 1481.

Details of crystal data collection. Data collection was performed at −100 °C with Mo

Kα radiation (λ = 0.71073 Å) on a Bruker SMART CCD equipped with a graphite

crystal, incident-beam monochromator. Lp and absorption corrections were applied to the

data. Both structures were solved by direct methods and refined by full-matrix least-

squares calculations with the *SHELXTL−PLUS* software package (Ver. 5.1).[1] One of the

coordinate dmf is statistically disordered. Two additional non-coordinating dmf sites

were observed, one of them was statistically disordered. Refinement of the structure

converged at a final $R1$ = 0.0591, $wR2$ = 0. 1490 for 5263 reflections of $I > 2\sigma(I)$, $R1$ =

0.1229, $wR2$ = 0. 1744 for all 9717 reflections. The largest difference peak and hole were

0.722 and −0.537 e·Å^{-3}, respectively. A summary of the crystal and intensity data is

given in Table S1.

References

(1) Sheldrick, G. M. *SHELXTL−PLUS*, *Crystal Structure Analysis Package*; Bruker

Analytical X-ray, Madison, WI, 1997.

Table S1. Crystal data and structure refinement for complex **1**.

|	
Empirical formula	$C_{216}H_{348}Mn_{12}N_{48}O_{60}$
Formula weight	5236.70
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	*R*-3
Unit cell dimensions	a = 23.7142(16) Å $\alpha = 90°$.
	b = 23.7142(16) Å $\beta = 90°$.
	c = 38.246(5) Å $\gamma = 120°$.
Volume	18626(3) $Å^3$
Z	3
Density (calculated)	1.401 Mg/m^3
Absorption coefficient	0.674 mm^{-1}
F(000)	8280
Crystal size	0.25 x 0.25 x 0.23 mm^3
Theta range for data collection	1.46 to 28.28°.
Index ranges	-31<=h<=18, -31<=k<=31, -49<=l<=50
Reflections collected	32464
Independent reflections	9717 [R(int) = 0.0913]
Completeness to theta = 28.28°	94.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8604 and 0.8496
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9717 / 42 / 589
Goodness-of-fit on F^2	0.936
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1490
R indices (all data)	R1 = 0.1229, wR2 = 0.1744
Largest diff. peak and hole	0.722 and -0.537 e.$Å^{-3}$
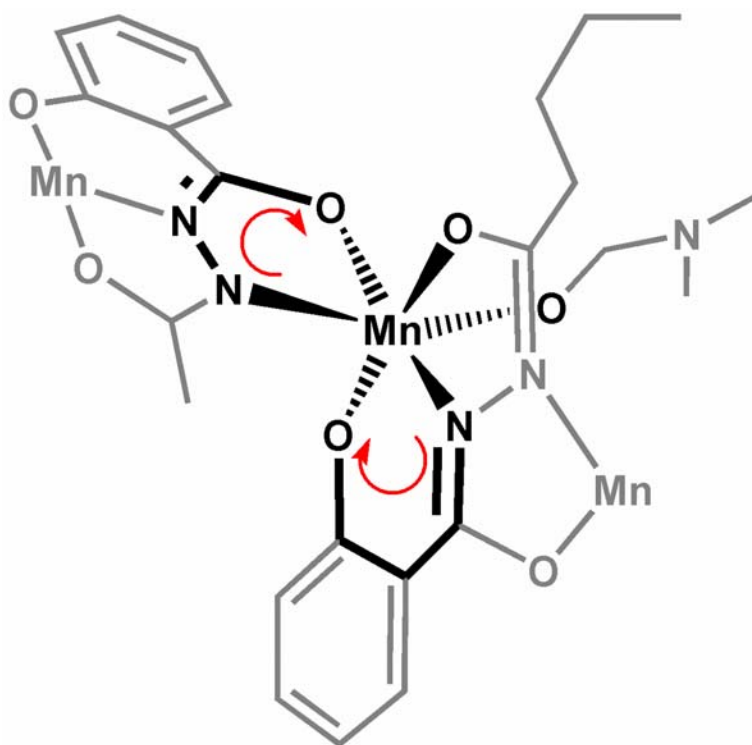
Figure S1. Schematic diagram showing Λ configuration of the central metal ion in the metalladiazamacrocycle.