Polyhedron 34 (2012) 24–30

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Syntheses and characterization of two supramolecular self-assembled Mn(II) compounds using *trans* 4,4′-azobispyridine as a bridging ligand: Effect of π–π interactions in the formation of a solid-state structure

Rajdip Dey, Debajyoti Ghoshal *

Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 27 October 2011
Accepted 2 December 2011
Available online 16 December 2011

Keywords:
X-ray diffraction
π–π Interaction
Manganese(II)
Thermal study

ABSTRACT

Two new compounds of Mn(II) with the same bridging ligand, *trans* 4,4′-azobispyridine (*azbpy*), and different co-ligands, 1,10-phenanthroline (*phen*) and 2,2′-bipyridine (*bpy*), have been synthesized and characterized by X-ray crystallography and other physicochemical methods. Although the compounds were prepared under similar reaction conditions, as well as using the same reactant ratios, their compositions and solid state structures are entirely different in the two cases. Compound **1**, with $[Mn(azbpy)(phen)Cl_2]_n$ and $[Mn(phen)_2Cl_2]$ moieties, constructs a supramolecular 3D self assembly through π–π interactions, whereas in **2** the $[Mn(azbpy)(bpy)Cl_2]_n$ moiety and the lattice *azbpy* forms the supramolecular 3D arrangement by both π–π and C–H···π interactions. A thermogravimetric study of the complexes and the solid state fluorescence spectra of the ligand and complexes corroborate their structures.

1. Introduction

The design of supramolecular self assemblies has had considerable attention over the last two decades, due to its structural elegancy as well as functional properties [1–8]. In this context, the effect of aromatic–aromatic interactions or π–π interactions [9,10] on the formation of supramolecular self assemblies has become important as these types of interactions are quite ubiquitous in the secondary and tertiary structures of proteins [11,12].

The effect of π–π interactions in the formation of highly fascinating supramolecular self-assemblies, even from very simple monomeric building blocks [13–17], has become an interesting area in crystal engineering [18,19]. This is also important as the controlled self-assembly of small molecules with well defined association properties is easier and more economical than the direct synthesis of a similarly complex covalent structure [20–26].

Hence, to investigate the effect of π–π interactions on crystal packing we have synthesized two compounds of Mn(II) with the same bridging ligand, *trans* 4,4′-azobispyridine (*azbpy*), and different co-ligands, 1,10-phenanthroline (*phen*) and 2,2′-bipyridine (*bpy*). Although the compounds were prepared under similar reaction conditions, as well as using the same reactant ratios, the solid state structures, and even the moiety formulae, are entirely different in the two cases. Compound **1**, with $[Mn(azbpy)(phen)Cl_2]_n$ and $[Mn(phen)_2Cl_2]$ moieties, forms a self assembly by π–π interactions only. Here the self-assembly is constructed by chains which are stacked with mononuclear units to create an overall supramolecular sheet type arrangement (Scheme 1). In **2**, the $[Mn(azbpy)(bpy)Cl_2]_n$ moiety along with lattice *azbpy* forms a three-leg ladder type arrangement, where the aromatic rings of the ligated bipyridine are stacked by strong face to face π–π interactions with the pyridine ring of lattice *azbpy* ligands (Scheme 2). The solid state structure of **2** is further extended into a 2D structure with C–H···π interactions.

2. Experimental

2.1. Materials

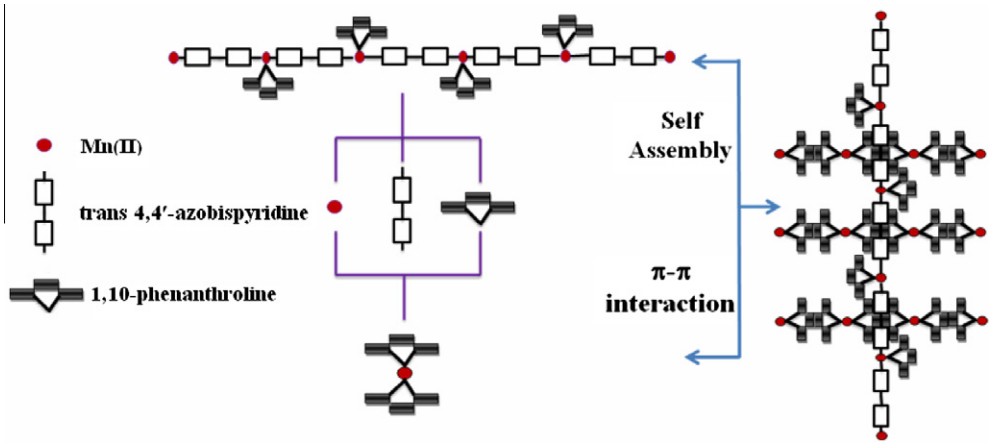
Trans 4,4′-azobispyridine (*azbpy*) was synthesized following a slightly modified published procedure of the oxidative coupling of 4-aminopyridine [27–29]. High purity manganese(II) chloride tetrahydrate was purchased from the Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade and used as received.

2.2. Physical measurements

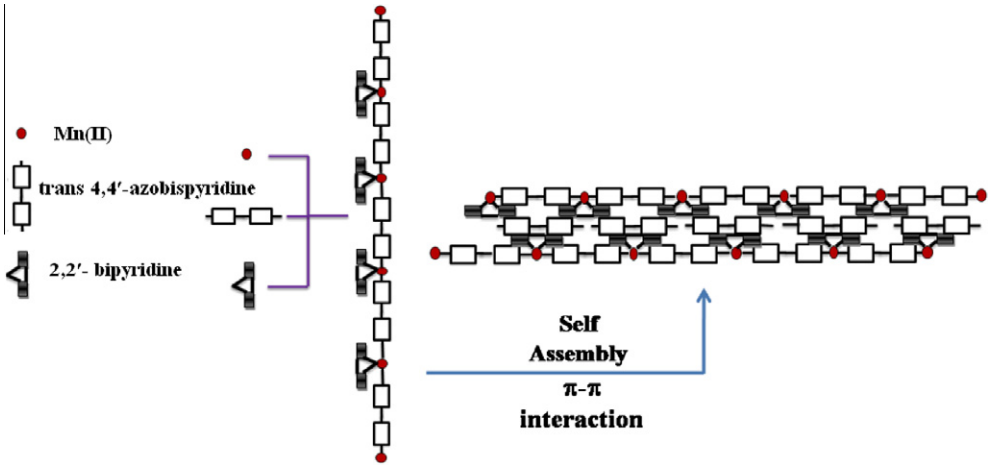
Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra (4000–400 cm^{-1}) were taken as KBr pellets, using a Perkin–Elmer Spectrum BX-II IR spectrometer. TGA was carried out on a Shimadzu DT-30 thermal analyzer under dinitrogen (flow

* Corresponding author. Fax: +91 3324146223.
E-mail address: dghoshal@chemistry.jdvu.ac.in (D. Ghoshal).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.12.004



Scheme 1.



Scheme 2.

Table 1
Crystallographic and structural refinement parameters for **1** and **2**.

	1	**2**
Formula	$C_{70}H_{62}N_{14}O_7Cl_6Mn_3$	$C_{30}H_{24}N_{10}Cl_2Mn$
Formula weight	1588.85	650.43
Crystal system	monoclinic	monoclinic
Space group	$P2/n$	$P2_1/m$
a (Å)	15.1295(5)	9.5490(7)
b (Å)	10.5555(4)	13.6792(10)
c (Å)	24.2910(9)	11.2541(9)
α (°)	90	90
β (°)	96.549(2)	91.402(4)
γ (°)	90	90
V (Å^3)	3853.9(2)	1469.60(19)
Z	2	2
D_{calc} (g cm^{-3})	1.357	1.470
μ (mm^{-1})	0.751	0.671
$F(000)$	1598	666
θ Range (°)	1.5–27.6	1.8–28.1
Reflections collected	51 105	13 015
Unique reflections	8898	3691
Reflections $I > 2\sigma(I)$	5779	3066
R_{int}	0.061	0.028
Goodness-of-fit (GOF) (F^2)	1.09	1.15
R_1 ($I > 2\sigma(I)$)[a]	0.0844	0.0655
wR_2 ($I > 2\sigma(I)$)[a]	0.2762	0.1620
$\Delta\rho$ maximum/minimum (e Å^3)	−0.67, 1.43	−0.41, 0.51

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**.

Mn1–Cl1	2.4599(13)	Mn1–N1	2.300(3)
Mn1–N3	2.333(3)	Mn1–Cl1a	2.4599(13)
Mn1–N1a	2.300(3)	Mn1–N3a	2.333(3)
Mn2–N7	2.266(5)	Mn2–Cl3	2.482(2)
Mn2–N4	2.329(4)	Mn2–Cl2	2.4202(15)
Mn2–N6	2.284(4)	Mn2–N5	2.275(5)
Cl1–Mn1–N1	93.92(8)	Cl2–Mn2–N7	93.45(12)
Cl1–Mn1–N3	163.46(9)	Cl3–Mn2–N4	164.53(11)
Cl1–Mn1–Cl1a	103.89(5)	Cl1–Mn1–N1a	91.33(8)
Cl1–Mn1–N3a	92.44(8)	Cl1a–Mn1–N1	91.33(8)
N1–Mn1–N3	88.21(11)	N1–Mn1–N1a	171.48(12)
N1–Mn1–N3a	84.87(11)	N3–Mn1–N3a	71.40(11)
Cl1a–Mn1–N3	92.44(8)	Cl3–Mn2–N5	94.96(12)
N1a–Mn1–N3	84.87(11)	Cl3–Mn2–N6	87.67(12)
Cl1a–Mn1–N1a	93.92(8)	Cl3–Mn2–N7	102.17(13)
Cl1a–Mn1–N3a	163.46(9)	N4–Mn2–N5	72.22(15)
N1a–Mn1–N3a	88.21(11)	N4–Mn2–N6	85.70(14)
N4–Mn2–N7	89.26(16)	N6–Mn2–N7	73.18(16)
N5–Mn2–N6	98.12(16)	Cl2–Mn2–N4	92.28(9)
N5–Mn2–N7	160.29(16)	Cl2–Mn2–N6	166.48(12)
Cl2–Mn2–Cl3	97.35(7)	Cl2–Mn2–N5	93.97(12)

Symmetry code: a = 1/2 − x, y, 1/2 − z.