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Crystallization Method Controlled Trinuclear or Ion-Pair Manganese(III)–Porphyrin-Based Heterobimetallic Complexes: Synthesis, Spectra Characterization, and Crystal Structure[1]

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Abstract—Cyanide-bridged trinuclear heterometallic Ag(I)–Mn(III) complex $\{[Mn(TClPP)(H_2O)]_2[Ag(CN)_2]\}_2 \cdot 2Br \cdot 2C_3H_6O \cdot 3H_2O$ (**I**) and ion-pair complex $\{[Mn(TClPP)(CH_3OH)_2][Ag(CN)_2]\} \cdot 0.5H_2O$ (**II**) have been synthesized with $[Mn(TClTPP)(H_2O)_2]Br$ ($H_2TClTPP$ = *meso*-tetra(4-chlorophenyl)porphyrin) as assembling segment and $K[Ag(CN)_2]$ as building block by using different crystallization method. These two complexes have been characterized by elemental analysis, IR spectroscopy and X-ray structure determination. In the trinuclear complex **I**, $[Ag(CN)_2]^-$ as bidentate ligand coordinates with the two central Mn(III) atom of $[Mn(TClPP)(H_2O)_2]^+$ through its two *trans* cyanide groups to form the complex cation of $[Mn(TClPP)(H_2O)]_2[Ag(CN)_2]^+$, which further constructs the neutral complexes with the help of one Br^- as balanced anion. For the ion-pair complex **II** composed by free $[Mn(TClPP)(CH_3OH)_2]^+$ cation and free $[Ag(CN)_2]^-$ anion, it can be linked into one-dimensional supramolecular structure with the dependence of the intermolecular O–H···N and O–H···O hydrogen bond interactions.

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INTRODUCTION

Since the discovery in the beginning of the last century, porphyrin derivatives have always attracted continuous and extensive research interest in a wide range of fields not only because of their excellent chemical and physical properties but also due to their affluent molecular structures associated with the easy peripheral modification over porphyrin rings based on several successful strategies [1–7]. As has been known, porphyrin as one of the most versatile ligands can coordinate with many metal magnetic centers including transition metals and rare earths as large equatorial plane or terminal capped ligand. In addition, the steric effect of porphyrins can be tuned through the peripheral substitution, which offers ideal carriers for the rational molecular design.

The manganese(III) porphyrin derivatives containing the magnetic center of Mn^{3+} ion caped by the porphyrin ligand usually manifests significant negative magnetic anisotropy, which is very favor of forming complexes with interesting magnetic properties, such as SMM or SCM [8–11]. Under this consideration, we started to pay attention on exploiting to construct cyanide-bridged magnetic complexes of manganese(III) porphyrin derivatives, and reported many low-dimensional cyanide-bridged manganese(III) porphyrin-based heterometallic complexes in our recent works [12–14]. In this paper, we present our further work about the cyanide-bridged manganese(III) porphyrin-based complexes which primarily concerns the synthesis, spectra characterization and crystal structures of a cyanide-bridged trinuclear heterometallic Ag(I)–Mn(III) complex $\{[Mn(TClPP)(H_2O)]_2[Ag(CN)_2]\}_2 \cdot 2Br \cdot 2C_3H_6O \cdot 3H_2O$ (**I**) and ion-pair complex $\{[Mn(TClPP)(CH_3OH)_2][Ag(CN)_2]\} \cdot 0.5H_2O$ (**II**) obtained from the reactions of $[Mn(TClTPP)(H_2O)_2]Br$ ($H_2TClTPP$ = *meso*-tetra(4-chlorophenyl)porphyrin) and $K[Ag(CN)_2]$ by using different crystallization method.

EXPERIMENTAL

Materials and methods. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region. All the reactions were carried out under an air atmosphere and all chemicals and solvents used were reagent grade without further purification. H_2TClPP was synthesized according to the Adler-Longo method [15].

Synthesis of $[Mn(TClPP)(H_2O)_2]Br$. The mixture of H_2TClPP and $MnBr_2$ with molar ratio of 1 : 1 in DMF was refluxed for 6–7 h in air. After the reaction was completed through TLC analysis, the mixture was cooled to room temperature and poured into ice cooled water. The resulting dark brown precipitate was separated by filtration and washed several times with

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cooled water, then dried in vacuum. The yield was 70–80%.

Synthesis of complex I. To a solution of $[Mn(TClPP)(H_2O)_2]Br$ (0.10 mmol, 92.1 mg) in methanol and acetone (10 mL, v/v = 1 : 1), $K[Ag(CN)_2]$ (0.10 mmol, 23.8 mg) dissolved in a minimum of water was carefully added. The resulting mixture was filtered at once and the filtrate kept undisturbed in the dark box at room temperature. After one week, dark brown block crystals were collected by filtration with the yield of 52.3 mg (53.05%).

For $C_{186}H_{122}Ag_2Br_2Cl_{16}Mn_4N_{20}O_9$ (**I**)

anal. calcd., %:	C, 54.65;	H, 3.12;	N, 7.10.
Found, %:	C, 54.52;	H, 3.21;	N, 7.02.

Main IR bands (ν, cm^{-1}): 2157 s ν(C≡N), 1625 v.s ν(C=N).

Synthesis of complex II. This complex was synthesized with the starting materials same to that for complex **I** by using diffusion method. A red-brown methanol and acetone solution (10 mL, v/v = 1 : 1) of $[Mn(TClPP)(H_2O)_2]Br$ (0.1 mmol, 92.1 mg) was carefully layered onto a colorless aqueous solution (10 mL) of $K[Ag(CN)_2]$ (0.1 mmol, 23.8 mg). After the mixture stood for a few days in the dark box, dark brown crystals suitable for X-ray diffraction were obtained. They were collected by filtration, washed with cooled methanol-water, and dried at room temperature with the yield of 41.9 mg (40.37%).

For $C_{48}H_{33}AgCl_4MnN_6O_{2.5}$ (**II**)

anal. calcd., %:	C, 55.52;	H, 3.20;	N, 8.09.
Found, %:	C, 55.39;	H, 3.06;	N, 8.01.

Main IR bands (ν, cm^{-1}): 2116 s ν(C≡N), 1627 v.s ν(C=N).

X-ray crystallography. Single crystals of complexes **I** and **II** for X-ray diffraction analyses with suitable dimensions were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a MoK_α sealed tube (λ = 0.71073 Å) at 293 K using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced as fixed contributors and assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C)$, and their coordinates were allowed to ride on their respective carbons using SHELXL-97. For the H atoms of the coordinated water (methanol) molecules and the solvent molecules, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. Details of the crystal parameters, data collection and refinement for complexes **I** and **II** are summarized in Table 1. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 957405 (**I**) and 957406 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	3943.56	1038.41
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	16.244(4)	11.1957(7)
b, Å	17.423(5)	19.9065(14)
c, Å	18.827(5)	22.2970(15)
α, deg	105.627(5)	103.4840(10)
β, deg	107.982(5)	97.9740(10)
γ, deg	92.596(5)	96.7580(10)
V, Å^3	4832(2)	4727.1(5)
Z	1	4
Completeness	98.2%	99.1%
F(000)	1986	2092
θ Range, deg	1.19–25.01	1.60–25.01
Reflections collected/ independent (R_{int})	23805/16745 (0.0496)	23661/16526 (0.0161)
Reflections with ($I > 2\sigma(I)$)	7575	11201
Parameters	1099	1133
GOOF	1.010	1.023
R_1 ($I > 2\sigma(I)$)	0.1193	0.0474
wR_2 (all data)	0.3539	0.1506
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.033/–0.894	0.975/–0.673

RESULTS AND DISCUSSION

Both of the two complexes were prepared with $K[Ag(CN)_2]$ as building block and $[Mn(TClPP)(H_2O)_2]Br$ as assemble segment. The trinuclear complex **I** was obtained by a slow evaporation method, while the ion-pair complex **II** was afforded by a diffusion method. The different structures of these two complexes indicate that the crystallization method can put obvious influence on the structure of the complex formed. These two complexes have been characterized by IR spectrum. In the IR spectra of cyanide-bridged complex **I**, one peak at ~2160 cm^{-1} due to the bridged cyanide-stretching vibration was observed. For the IR spectra of complex **II**, only one single peak at ~2116 cm^{-1} was observed, confirming the absence of bridging cyanide group in this complex.

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I		**II**	
Mn(1)–N(1)	2.222(10)	Mn(1)–N(1)	1.995(3)
Mn(1)–N(2)	1.989(8)	Mn(1)–N(2)	2.014(3)
Mn(1)–N(3)	2.004(8)	Mn(1)–N(3)	2.006(3)
Mn(1)–N(4)	2.002(8)	Mn(1)–N(4)	2.020(3)
Mn(1)–N(5)	2.005(8)	Mn(1)–O(2)	2.255(3)
Mn(1)–O(4)	2.311(9)	Mn(1)–O(3)	2.218(3)
Angle	ω, deg	Angle	ω, deg
I		**II**	
C(17)Ag(1)C(17)$^{\#1}$	180.000(1)	C(91)Ag(1)C(92)	177.3(2)
C(23)N(1)Mn(1)	170.0(10)	C(94)Ag(2)C(93)	171.1(2)
C(17)N(6)Mn(2)	171.4(10)	O(3)Mn(1)O(2)	178.24(11)

* Symmetry transformations used to generate equivalent atoms for complex **I**: $^{\#}$ $-x+1, -y+1, -z$; $^{\#2}$ $-x+2, -y+1, -z+2$.

Some important structural parameters for the title complex are collected in Table 2. The cationic structure for the complex **I** and its cell packing diagram are shown in Figs. 1 and 2, respectively. For complex **II**, its neutral ion-pair structure and 1D supramolecular structure formed by intermolecular hydrogen bond interactions are given in Fig. 3.

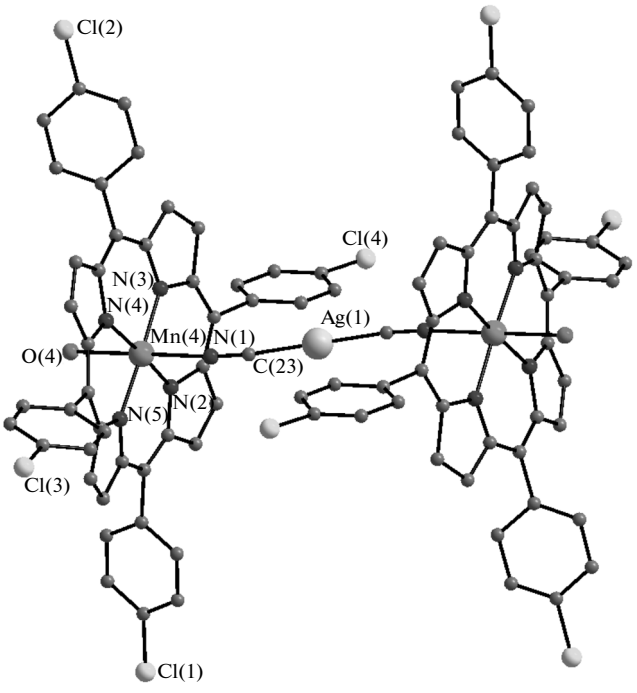

Fig. 1. The cationic structure for the complex **I**. All the H atoms, the solvent molecules and the balanced Br^- have been omitted for clarity.

As can be found, complex **I** crystallizes in triclinic space group $P\bar{1}$, containing two independent trinuclear units in the unit cell. Complex **I** is composed of cationic trinuclear entity with the formula of $\{[Mn(TClPP)(H_2O)]_2[Ag(CN)_2]\}^+$ and B^- acting as balance cation. The cyanide building block $[Ag(CN)_2]^-$ with a well linear conformation acts as bidentate ligand through its two *trans* cyanide groups towards two central Mn^{3+} ion of two manganese(III) porphyrin units. The coordination sphere for the Mn atom is a distorted octahedral, in which four equatorial positions are occupied by four pyrrole N atoms and the other two axial ones come from the N atom of the bridging cyanide group and the O atom of the coordinated water molecule. As shown in Table 2, the distances between Mn atom and the pyrrole N atoms 1.989(8), 2.002(8), 2.004(8) and 2.005(8) Å are obviously shorter than the $Mn-N_{cyanide}$ and $Mn-O_{H_2O}$ bond lengths with the values 2.222(10) and 2.311(9) Å, which gives further information about the elongation octahedron surrounding the Mn^{3+} ion, typically accounting for the well known Jahn-Teller effect. The angles of C≡N–Mn in complex **I** are very close to 170°, indicating that these three atoms deviates slightly from a linear configuration.

Complex **II** crystallizes also in triclinic space group $P\bar{1}$ and contains free $\{[Mn(TClPP)(CH_3OH)_2]^+$ cation and $[Ag(CN)_2]^-$ anion. The Ag–C bond lengths and the Ag–C≡N bond angles are almost equal to those corresponding parameters in complex **I**, demon-

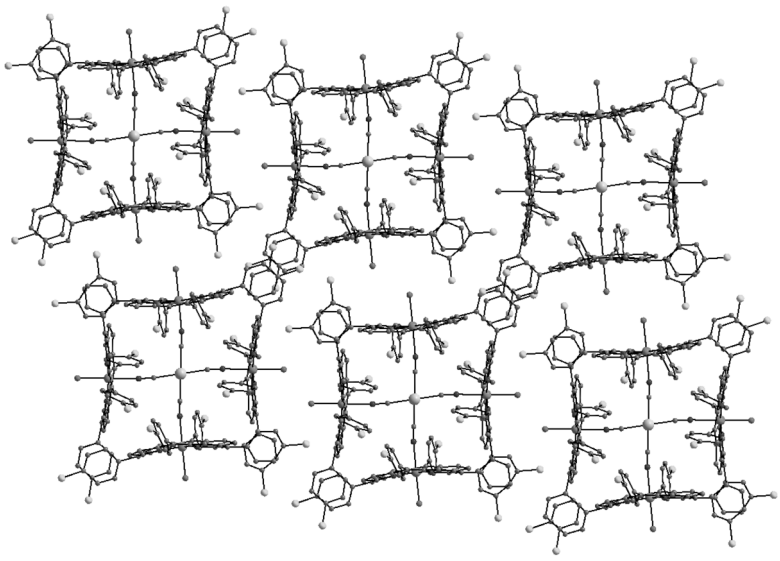

Fig. 2. The cell packing diagram of complex **II** along *x* axis. All the H atoms, the solvent molecules and the balanced Br^- have been omitted for clarity.

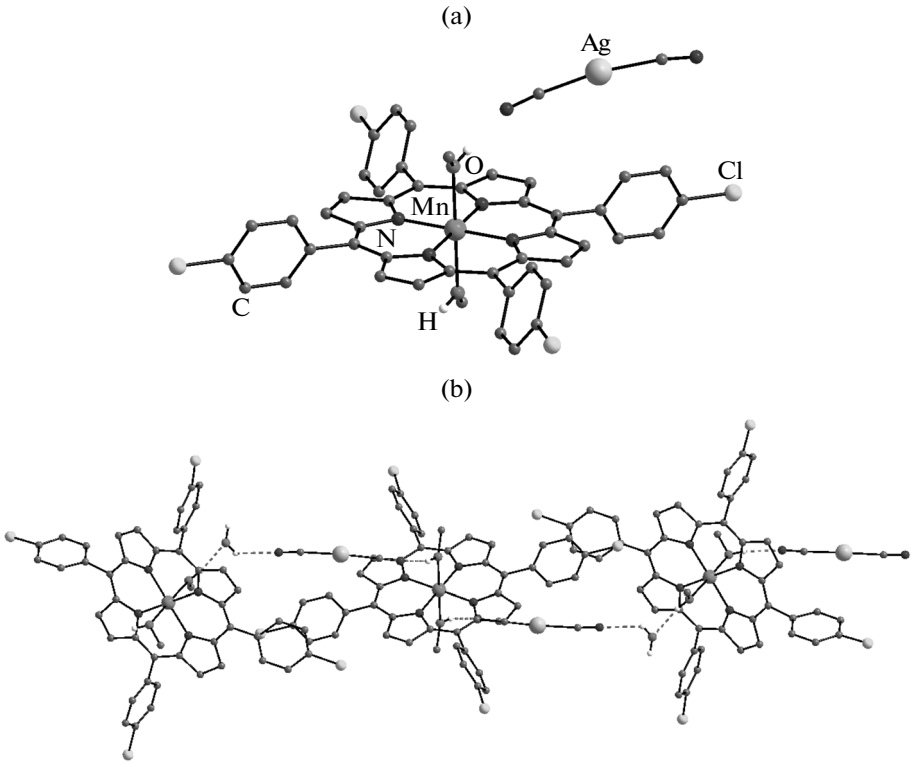

Fig. 3. The ion-pair structure complex **II** (a) and its 1D supramolecular structure formed by intermolecular hydrogen bond interactions (b). All the H atoms except those used to form H-bond interactions have been omitted for clarity.

strating that the coordinating or non-coordinating of the N atom to the metal atom has no obvious influence on the geometry of the cyanide precursor. Same to that in complex **I**, the coordination sphere of the Mn(III) atom coordinated by a N_4O_2 unit is also a distorted octahedron. As shown in Fig. 3, one-dimensional

supramolecular structure can be formed under the help of the intermolecular O–H···O and O–H···N hydrogen bond interactions.

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