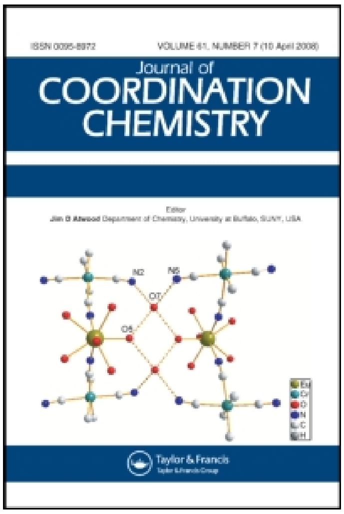

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# Two 1-D metal-organic polymers constructed from bis-benzimidazole-based ligands: syntheses, crystal structures, and luminescent properties

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# Two 1-D metal-organic polymers constructed from bis-benzimidazole-based ligands: syntheses, crystal structures, and luminescent properties

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By combination of Mn(II) and Hg(II) salts with a flexible building unit 1,1′-(1, 5-pentanediyl)-*bis*-1H-benzimidazole (pbbm), two 1-D chain metal-organic polymers $[Mn(SCN)_2(pbbm)_2]_n$ (**1**) and $\{[HgCl_2(pbbm)] \cdot DMF\}_n$ (**2**) have been prepared. The polymeric 1-D chains in **1** consist of parallel ribbons of rings, whereas **2** possesses a 1-D zig-zag chain framework based on tetrahedral mercury atoms bridged by pbbm molecules and terminally coordinated by two chlorides. The significant differences of these metal-organic frameworks indicate that the flexible pbbm ligand adjusts its conformation to meet the requirement of the coordination preference of the metal center. The photoluminescent properties of these new materials have been studied in the solid state at room temperature.

*Keywords*: Metal-organic polymer; Self-assembly; Chain structure; Fluorescence

## 1. Introduction

Crystal engineering of metal-organic frameworks (MOFs) has attracted great interest for both the structural and topological novelty along with potential applications in many areas [1, 2]. In such materials, functionality can be introduced from either the inorganic species or the organic building blocks. Furthermore, the combination produces cooperative effects so as to enhance the properties. The structural motifs of these molecular assemblies are closely related to the geometries of metal centers and organic ligands. Careful selection of a suitable, multifunctional, organic ligand with features such as flexibility and versatile bonding modes is helpful for constructing and tailoring these species [3]. Even so, rational control over desired topologies and properties is still a challenge because the self-assembly process is influenced by subtle factors from crystallization, such as counter-anion, temperature, the solvent used, etc. [4, 5]. Therefore, more research is indispensable to gain information of the

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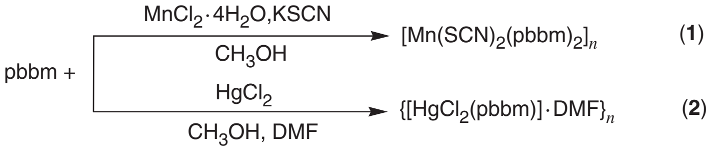
relevant structural types and establish the proper correlation between structures and properties.

The $Mn^{2+}$ ion with a $d^5$ valence shell is well-suited because of its labile coordination modes and counter-anions, such as $Cl^-$ or $SCN^-$, which can be incorporated as an essential element of the framework. This offers the possibility for constructing various nuclearities and structural complexity. As a $d^{10}$ metal ion, $Hg^{2+}$ is also particularly useful for coordination frameworks. The spherical $d^{10}$ configuration is associated with a flexible coordination environment with geometries varying from tetrahedral to octahedral; severe distortions in the ideal polyhedra occur easily. Moreover, the general lability of $d^{10}$ metal ion complexes makes formation of coordination bonds reversible enabling metal ions and ligands to rearrange during polymerization to give highly ordered network structures. Consequently, $Hg^{2+}$ can readily accommodate all kinds of architectures and 1-D, 2-D and 3-D polymers. For instance, Chen and co-workers have succeeded in preparing a 3-D network metal-organic coordination polymer $[Mn(bct)(H_2O)(4,4'\text{-bipy})]$ ($H_2bct = 2,5$-*bis*(carboxymethylmercapto)-1,3,4-thiadiazole acid) [6]. Mukherjee *et al.* reported a zig-zag 1-D chain $[Mn(H_2bpbn)_{1.5}][ClO_4]_2 \cdot 2MeOH \cdot 2H_2O$ ($H_2bpbn = N,N'$-*bis*(2-pyridinecarboxamido)-1,4-butane) [7]. $[HgI_2(bpt)]_2$, $[MnCl_2(bpt)_2]_n \cdot 2CH_3OH$ (bpt = $N,N'$-*bis*(3-pyridylmethyl)thiourea) [8a], $[Hg(tmp)I_2]_n$ (tmp = 4,4′-trimethylene dipyridine) and $[Hg(azobpy)I_2]_n$ (azobpy = 3,3′-azobispyridine) [8b] have a 2-D supramolecular network, 1-D double chain, 1-D wave-shaped chain as well as a 3-D supramolecular framework, respectively. For some time, we have focused our efforts on design and preparation of *bis*-benzimidazole-type bridging ligands, which exhibited ability to join metal ions to offer a variety of inorganic–organic arrangements ranging from discrete assemblies to infinite molecular networks [9,10]. These structurally varied architectures provide insight into the design of solid-state materials. To further probe the versatility of 1,1′-(1,5-pentanediyl)*bis*-1H-benzimidazole (pbbm) [10a] to construct $Mn^{2+}$ and $Hg^{2+}$-containing MOFs, as well as structural consequences on materials of such systems, self-assembly reactions are carried out in solution, and $[Mn(SCN)_2(pbbm)_2]_n$ (**1**) and $\{[HgCl_2(pbbm)] \cdot DMF\}_n$ (**2**) obtained (scheme 1).



Scheme 1. Synthetic routes for **1** and **2**.

## 2. Experimental

### 2.1. *Materials and measurements*

All chemicals were of A.R. Grade and used without purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 $cm^{-1}$ region. Carbon, hydrogen, and nitrogen analyses were carried out on a FLASH EA 1112 elemental analyzer. The luminescence spectra were measured on powder samples at room temperature using a F-4500 HITACHI fluorescence spectrophotometer. The excitation slit was 5 nm and the emission slit was also 5 nm, the response time was 2 s pbbm was prepared according to the literature [10a].

### 2.2. *Synthesis of* $[Mn(SCN)_2(pbbm)_2]_n$ *(1)*

A methanol solution (5 mL) of pbbm (30.4 mg, 0.1 mmol) was added to aqueous solution (4 mL) of $MnCl_2 \cdot 4H_2O$ (9.9 mg, 0.05 mmol) and KSCN (9.7 mg, 0.1 mmol) to give a clear solution. Prismatic colorless crystals (58% yield) suitable for X-ray diffraction were obtained 1 week later. The crystals are air-stable and dissolved in $CHCl_3$, $CH_3CN$, and DMF. Anal. Calcd for $C_{40}H_{40}MnN_{10}S_2$: C, 61.60; H, 5.17; N, 12.96%. Found: C, 61.58; H, 5.18; N, 12.93%. IR (KBr) $cm^{-1}$: 3111 m, 2938 m, 1610 w, 1597 s, 1519 s, 1457 s, 1391 w, 1298 m, 749 s, 612 w.

### 2.3. *Synthesis of* $\{[HgCl_2(pbbm)] \cdot DMF\}_n$ *(2)*

A methanol solution (6 mL) of pbbm (30.4 mg, 0.1 mmol) was carefully laid on a DMF solution (4 mL) of $HgCl_2$ (27.15 mg, 0.1 mmol). Red crystals (62% yield) suitable for X-ray diffraction were obtained 3 days later. Anal. Calcd for $C_{22}H_{27}Cl_2HgN_5O$: C, 40.72; H, 4.19; N, 10.79%. Found: C, 40.73; H, 4.21; N, 10.77%. IR (KBr) $cm^{-1}$: 3107 m, 2939 m, 1504 s, 1459 m, 1296 w, 1249 s, 761 s, 633 w.

### 2.4. *X-ray structure analyses*

Data collection was performed on a Rigaku RAXIS-IV image plate area detector using graphite-monochromated Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation at 291(2) K using the $\omega$–$2\theta$ scan technique. The data were corrected for Lorentz and polarization factors and for absorption by using empirical scan data. The structure was solved with the *SHELX* program [11] and refined by full-matrix least-squares methods based on $F^2$, with anisotropic thermal parameters for the nonhydrogen atoms. H atoms on C atoms are placed in calculated positions and refined in the riding model approximation with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}$ (C). Crystal data and structure refinement of **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

## 3. Results and discussion

### 3.1. *Structure of* $[Mn(SCN)_2(pbbm)_2]_n$ *(1)*

Single-crystal structure determination reveals that **1** crystallizes in the monoclinic space group *P*2(1)/*n* with a neutral asymmetric unit $[Mn(SCN)_2(pbbm)_2]$ with infinite 1-D double-stranded chains that can be described as ribbons of rings. The structure consists of homometallic manganese chains linked by double pbbm bridges. As illustrated in figure 1(a), the Mn(II), being located at an inversion center, is six-coordinate with four

Table 1. Crystal data and structure refinement for $[Mn(SCN)_2(pbbm)_2]_n$ (**1**) and $\{[HgCl_2(pbbm)] \cdot DMF\}_n$ (**2**).

| | **1** | **2** |
|---|---|---|
| Formula | $C_{40}H_{40}MnN_{10}S_2$ | $C_{22}H_{27}Cl_2HgN_5O$ |
| Formula weight | 779.88 | 648.98 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2(1)/n$ | $P2(1)/n$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 9.1083(18) | 11.677(2) |
| $b$ | 21.884(4) | 14.266(3) |
| $c$ | 9.6968(19) | 14.752(3) |
| $\alpha$ | 90 | 90 |
| $\beta$ | 101.58(3) | 95.06(3) |
| $\gamma$ | 90 | 90 |
| V (Å$^3$) | 1893.4(7) | 2447.9(9) |
| T(K) | 291(2) | 291(2) |
| Z | 2 | 4 |
| μ(Mo-K$\alpha$) (cm$^{-1}$) | 1.368 | 2.178 |
| Number of reflections collected [$I > 2\sigma(I)$] | 2895 | 3917 |
| Number of independent reflections | 2281 | 2641 |
| Final $R^a$, $R_w{}^b$ | 0.0524,0.1377 | 0.0354,0.0596 |

Note: $^aR = \sum \|.F_0|. - |.F_c\|./\sum |F_0|.$
$^bR_w = [\sum (\|.F_0|. - |.F_c\|.)^2/\sum{}_w|F_0|^2]^{1/2}..$

Table 2. Selected bond distances (Å) and angles (°).

| | | | | | |
|---|---|---|---|---|---|
| $[Mn(SCN)_2(pbbm)_2]_n$ (**1**) | | | | | |
| Bond distances | | | | | |
| Mn1–N1 | 2.345(3) | Mn1–N4 | 2.286(3) | Mn1–N5 | 2.199(3) |
| Bond angles | | | | | |
| N5–Mn1–N5 | 180.0 | N5–Mn1–N4 | 87.32(11) | N5–Mn1–N4 | 92.68(11) |
| N5–Mn1–N1 | 93.10(12) | N5–Mn1–N1 | 86.90(12) | N1–Mn1–N1 | 180.0 |
| N4–Mn1–N1 | 85.13(10) | N4–Mn1–N1 | 94.87(10) | N4–Mn1–N4 | 180.00(12) |
| $[HgCl_2(DMF)]_n$ (**2**) | | | | | |
| Bond distances | | | | | |
| Hg1–N1 | 2.276(5) | Hg1–N4 | 2.317(5) | Hg1–Cl1 | 2.395(2) |
| Hg1–Cl2 | 2.4337(19) | | | | |
| Bond angles | | | | | |
| N1–Hg1–N4 | 97.19(19) | N1–Hg1–Cl1 | 113.88(16) | N4–Hg1–Cl1 | 110.16(16) |
| N1–Hg1–Cl2 | 105.46(14) | N4–Hg1–Cl2 | 100.93(16) | Cl1–Hg1–Cl2 | 125.02(7) |

N donors from different imidazole rings of four individual pbbm ligands and two N atoms from isothiocyanate (NCS–) groups in a nearly ideal octahedron with N1A, N1AA, N4B, N4BA composing the basal plane (the mean deviation from plane of 0 Å) and N5A, N5AA holding axial positions. The bond angles around Mn(II) vary from 85.13(10) to 180.00(12)°, and $Mn–N_{pbbm}$ bond lengths [2.286(3), 2.345(3) Å] are longer than those of $Mn–N_{NCS}$ [2.199(3) Å]. The Mn(II)–N distances correspond to those observed in $[Mn_2(nbdoa)_2(2,2'\text{-bpy})_2]_n$ [Mn–N 2.2943(11), 2.3266(11) Å] [nbdoa$^{2-}$ = 2-nitro-benzene-1, 4-di(oxyacetate)] [12], $[Mn(H_2bpbn)_{1.5}][ClO_4]_2 \cdot 2MeOH \cdot 2H_2O$ [Mn–N 2.257(5) Å] [$H_2bpbn$ = $N,N'$-bis(2-pyridinecarboxamido)-1,4-butane] [13], $Mn(dmbpy)_2(OCN)_2$ [Mn–N 2.290(5)–2.341(5) Å] and $Mn(dmbpy)_2(dca)_2$ [Mn–N 2.168(3)–2.296(2) Å] (dmbpy = 4, 4′-dimethyl-2, 2′-bipyridine, dca = dicyanamide) [14].

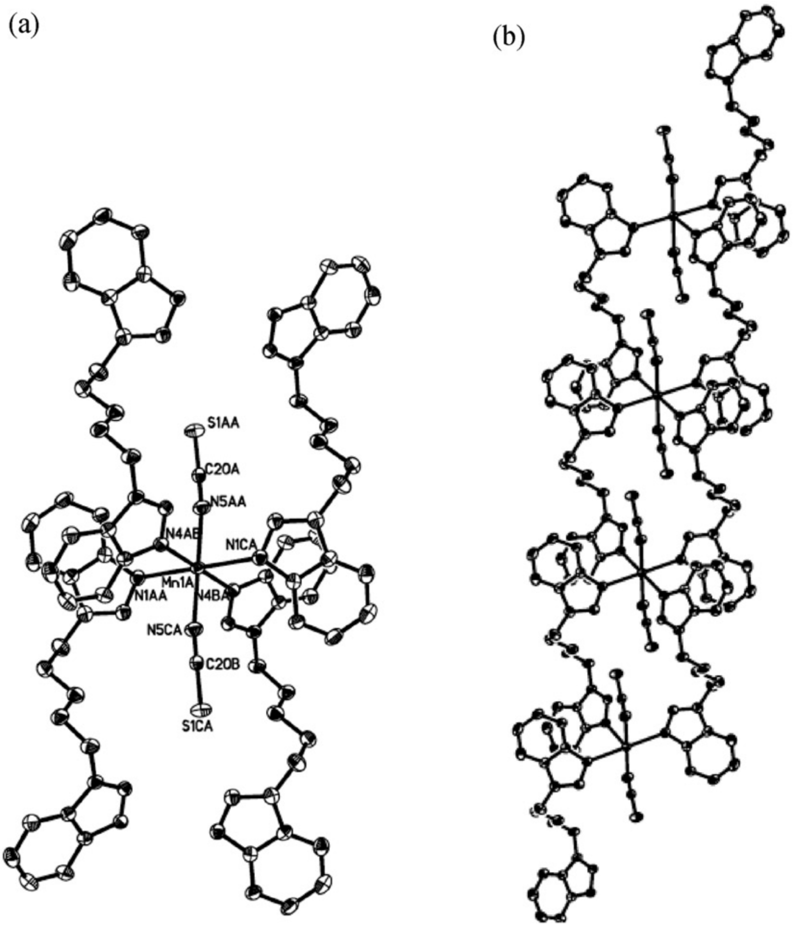


Figure 1. (a) The ORTEP representation for **1** with atom-labeling scheme; (b) The 1-D double-strand of **1**.

The two benzimidazole rings from the same pbbm are not coplanar, and the dihedral angle is 35.8°. These ligands twist to meet the requirement of steric exclusion. The torsion angles are −76.3(5)° and −73.0(4)° for N2–C8–C9–C10 and C10–C11–C12–N3, respectively. Each pair of twisted crystallographically independent pbbm ligands joins two adjacent Mn(II) centers to afford a ribbon of $Mn(pbbm)_2Mn$ 24-membered cycle in which the Mn(II) centers are separated by a distance of 9.697 Å. All these ribbons run parallel to the $\beta$ direction [figure 1(b)]. The ribbons of rings represent a common type of coordination polymer, previously observed in $\{[Cd(NO_3)(pbbm)_2]_2 \cdot (NO_3)_2 \cdot H_2O\}_n$, $[CdSO_4(pbbm)_2]_n$ [9(c)], $[Ni(H_2O)_2(dadpm)_2]Cl_2$ (dadpm = 4, 4′-diaminodiphenylmethane) and $[Co(bix)_2(H_2O)_2](SO_4) \cdot 7H_2O$ (bix = 1, 4-*bis*(imidazol-1-ylmethyl)benzene) [15].

### 3.2. *Structure of* $\{[HgCl_2(pbbm)] \cdot DMF\}_n$ *(2)*

In contrast to **1**, **2** displays a 1-D zig-zag chain structural motif (figure 2). The Hg(II) center is tetrahedrally coordinated by two nitrogens from different pbbm ligands and

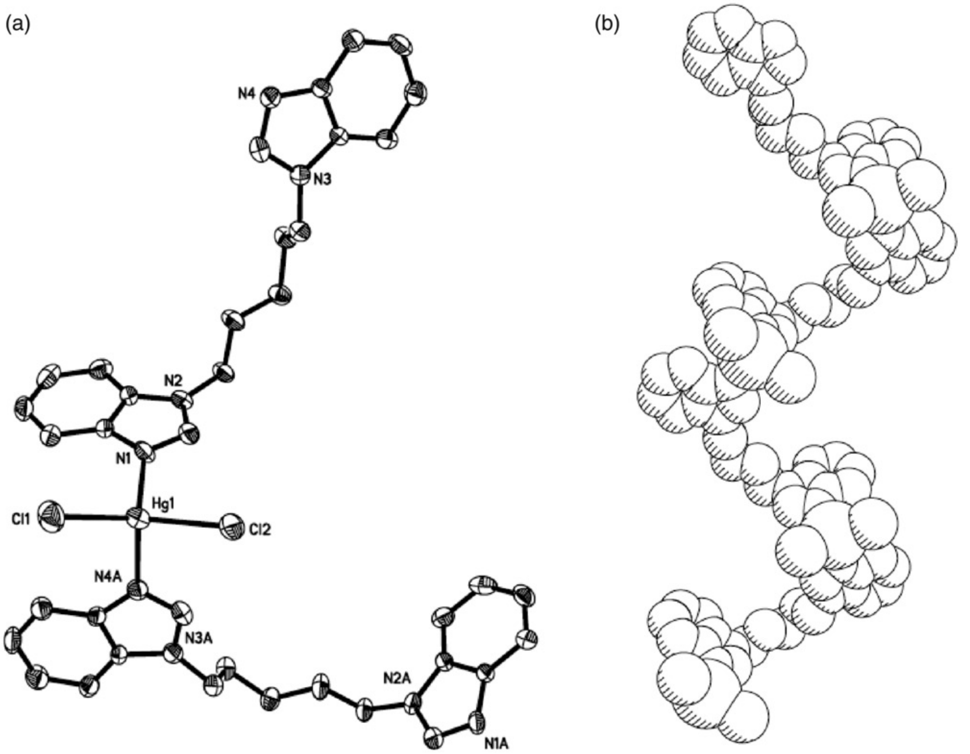


Figure 2. (a) The ORTEP representation for **2** with atom-labeling scheme; (b) The space-filling representation of 1-D zig-zag chain of **2**.

two terminal chlorides. The N–Hg–Cl bond angles range from 100.93(16) to 113.88(16)°, the Cl–Hg–Cl bond angle is 125.02(7)°, and the N–Hg–N bond angle is only 97.19(19)°. This distortion leads to a significant difference between two Hg-N bond lengths [2.276(5) and 2.317(5) Å] and Hg–Cl bond lengths [2.395(2) and 2.4337(19) Å], which are normal compared to other Hg(II) systems [8b, 16]. The deviation from the tetrahedron is probably caused by the preference for soft donors such as $Cl^-$ and weak preference for N atoms [17]. The pbbm ligand is twisted with the torsion angles of 172.0(5)° and −173.8(6)° for N2–C8–C9–C10 and C10–C11–C12–N3, respectively, and the dihedral angle between two benzimidazole planes is 100.2°, different from those found in **1**. This suggests that the flexible pbbm ligand can meet the geometrical requirement of metal ions through changing conformation adjusting the structure of the resulting products. Each *trans*-pbbm binds with two Hg(II) ions via nitrogens into a 1-D zig-zag chain running along the *b*-axis. The intrachain Hg–Hg separation is 13.206 Å.

### 3.3. *Photoluminescent properties of (1) and (2)*

Metal-organic polymers have the ability to affect emission wavelength and intensity of organic material through coordination [18]. Therefore, it is important to investigate the luminescent properties of metal-organic polymers in view of potential applications.

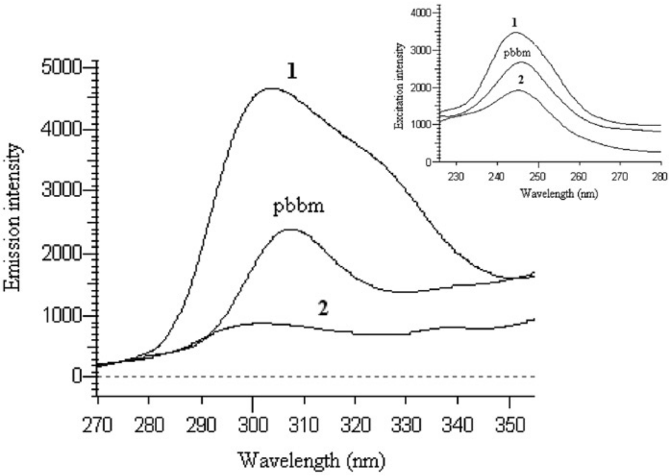


Figure 3. Excitation and emission spectra of **1** and **2** and pbbm in solid state at room temperature.

The photoluminescent behaviors of **1** and **2** and free ligand pbbm are studied in the solid state at room temperature. The excitation and emission spectra of **1** and **2** and pbbm are depicted in figure 3. Excitation at 245 nm leads to broad fluorescence signals with emission maxima at ~307 nm for free pbbm and 302 nm for **1** and **2**. The resemblance between the emission spectra of the two polymers and that of pbbm, excluding the emission intensity, indicates that the fluorescence of the polymers is pbbm based. Compared with the emission spectrum of pbbm, a slightly blue shift of 5 nm in both **1** and **2** is considered to arise from coordination of metal to ligand. Incorporation of MnII effectively increases the conformational rigidity of ligand and reduces the loss of energy via vibration. Thus, enhanced fluorescence intensity of **1** is detected. However, the significantly weakened intensity of the emission bands for **2** is attributed to the competitive quenching effect of halide ions [19]. The possible explanation for the difference emission properties of **1** and **2** is the different metal ions and coordination environment around them because the photoluminescence behavior is closely associated with the metal ions and ligands [20].

## 4. Conclusion

The isolation of two new MOFs clearly demonstrates the subtle interplay of ligand geometry, metal coordination preferences, and other factors in the formation of framework materials. The structure-function relationships of such components will begin to emerge and provide further guidelines for synthetic methodologies.

## Supplementary material

CCDC 685704 and 685705 for **1** and **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

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