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Crystal structure and characterization of two cadmium(II) coordination polymers with a multidentate N-donor tecton 3-(pyridin-4-yl)-5-(pyrazin-2-yl)-1H-1,2,4-triazole

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Crystal structure and characterization of two cadmium(II) coordination polymers with a multidentate N-donor tecton 3-(pyridin-4-yl)-5-(pyrazin-2-yl)-1H-1,2,4-triazole

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Two new cadmium(II) complexes $[Cd_{1.5}(L)Cl_2(H_2O)]_{2n}$ (**1**) and $[CdL_2]_n$ (**2**) with a multidentate N-donor building block 3-(pyridin-4-yl)-5-(pyrazin-2-yl)-1H-1,2,4-triazole (HL) have been prepared and characterized by elemental analysis, infra-red spectra, powder X-ray diffraction (XRD), and single-crystal XRD. **1** is a 2-D layered coordination polymer constructed from linkage of $[Cd_3(\mu\text{-}Cl)_4]$ trinuclear units with HL spacers, while **2** shows a 2-D layer structure. 3-D supramolecular architectures are further assembled in **1** and **2** *via* hydrogen-bonding contacts. Both **1** and **2** are thermally stable to 450 °C, and **2** showed strong fluorescent emission bands.

Keywords: Cd(II) coordination polymers; Crystal structure; Fluorescence; Supramolecular architecture

1. Introduction

Within the rapid development of crystal engineering, the rational design and construction of coordination architectures is a fertile research area, and increasing interest is evolving in view of their fascinating structural features and potential applications to gas storage, ion exchange, catalysis, *etc.* [1–5]. Diverse network architectures and physicochemical properties for such crystalline solids essentially depend on the metal ions and organic ligands used in the synthetic processes. In this regard, the proper combination of the inorganic and organic building components, that is, metal ions and ligands will basically be responsible for the resulting coordination architectures with desired structures and properties. Thus, rational selection of metal centers and organic ligands with suitable shape, functionality, flexibility, and symmetry plays a pivotal role in the synthesis of coordination polymers with desired structures and properties. Multidentate N-donor or O-donor ligands have been employed extensively in construction of extended structures. Among various ligands, imidazoles [6–9], polycarboxylates [10–13], and their derivatives have attracted attention

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for constructing a series of metal organic materials. Triazole and its derivatives are potential multitopic ligands in construction of coordination complexes. 3,5-Di-2-pyridyl-1,2,4-triazole [14], 3,5-bis(4-pyridyl)-4-(3-pyridyl)-1,2,4-triazole [15], 2,5-bis(4-pyridyl)-1,2,4-triazole [16], and 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole [17,18] have all been investigated. These ligands are bifunctional building blocks, in which the different regiochemical profiles of the 4-pyridyl, 3-pyridyl, and 2-pyridyl groups lead to different coordination and hydrogen-bonding interactions and therefore various structural motifs. In this contribution, we have investigated a pyridine and pyrazine-substituted triazole tecton, 3-(pyridin-4-yl)-5-(pyrazin-2-yl)-1H-1,2,4-triazole (HL), which is an angular pyridyl–pyrazinyl ligand that may show different conformations depending on the conditions used for constructing metal-organic frameworks. Coordination of pyridine and pyrazine substituted triazole to metal ions has only been the subject of limited study, and to our knowledge, only two examples with HL have been reported [19,20]. Thus, we carried out the reactions of HL with $CdCl_2{\cdot}2.5H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ and isolated two coordination polymers $[Cd_{1.5}(L)Cl_2(H_2O)]_{2n}$ (**1**) and $[CdL_2]_n$ (**2**), respectively. We report herein the crystal structures, which are directed by different anions used in the assembly processes, thermal stabilities and fluorescence spectra of **1** and **2**.

2. Experimental

2.1. *Materials and physical measurements*

All reagents used in the syntheses were of analytical grade. 3-(Pyridin-4-yl)-5(pyrazin-2-yl)1H-1,2,4-triazole (HL) was purchased from Jinan Henghua Sci. and Tec. Co. Ltd and used without purification. Elemental analyzes of C, H, and N were performed on a Vario-Elementar PE-2400 elemental analyzer. Thermogravimetric (TG) measurements were carried out in a nitrogen stream using a Netzsch STA449C apparatus with a heating rate of $10\,°C\,min^{-1}$. Fluorescence spectra were collected on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. X-ray power diffractometer data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA with Cu-Kα radiation (λ = 1.5406 Å), with a scan speed of $2\,°C\ min^{-1}$ and a step size of 0.02° in 2θ.

2.2. *Synthesis of the polymers*

2.2.1. Synthesis of $[Cd_{1.5}(L)Cl_2(H_2O)]_{2n}$ (1). A mixture of $CdCl_2{\cdot}2.5H_2O$ (0.5 mmol, 114 mg), HL (0.5 mmol, 188 mg), DMF (2 mL), and H_2O (8 mL) was stirred for 20 min in air, then transferred to a 25 mL Teflon-lined stainless vessel. The reaction was held at 150 °C for 3 days under autogenous pressure and then cooled to room temperature at $5\ °C\ h^{-1}$. The colorless block crystals of **1** (0.089 g, 55% yield) were collected. Anal. Calcd for $C_{11}H_9Cd_{1.50}Cl_2N_6O$ (%): C, 27.48; H, 1.89; N, 17.48. Found (%): C, 27.37; H, 1.86; N, 17.54.

2.2.2. Synthesis of $[CdL_2]_n$ (2). The same synthetic method as that for **1** was used except that $CdCl_2{\cdot}2.5H_2O$ was replaced by $Cd(NO_3)_2{\cdot}4H_2O$. The colorless block crystals of **2** (0.125 g, 45% yield) were collected. Anal. Calcd for $C_{22}H_{14}CdN_{12}$ (%): C, 47.28; H, 2.52; N, 30.08. Found (%): C, 47.45; H, 2.49; N, 30.12.

2.3. *Crystal structure determination*

Crystallographic data collections for **1** and **2** were carried out on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and

Table 1. Crystallographic and structure refinement data for **1** and **2**.

Empirical formula	$C_{11}H_9Cd_{1.50}Cl_2N_6O$	$C_{22}H_{14}CdN_{12}$
Formula weight	480.74	558.85
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C2/c*
Unit cell dimensions	$a = 7.4259(10)$ Å $\alpha = 90.092(2)°$	$a = 8.2691(9)$ Å
	$b = 8.0297(11)$ Å $\beta = 90.675(2)°$	$b = 11.0159(11)$ Å
	$c = 12.5620(17)$ Å $\gamma = 111.632(2)°$	$c = 23.243(2)$ Å
		$\beta = 97.782(2)°$
Volume, *Z*	696.23(16) Å^3, 2	2097.7(4) Å^3, 4
Calculated density (kg/m^3)	2.293	1.770
θ Range for data collection (°)	1.62 −25.09	1.77–25.10
Reflections collected/unique	3497/2454 [$R_{int} = 0.0222$]	5138/1868 [$R_{int} = 0.0239$]
Goodness-of-fit on F^2	1.112	1.051
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0963$	$R_1 = 0.0261$, $wR_2 = 0.0775$
R indices (all data)	$R_1 = 0.0365$, $wR_2 = 0.1055$	$R_1 = 0.0305$, $wR_2 = 0.0912$
Largest diff. peak, and hole	1.168 and −1.502 e Å^{-3}	0.438 and −0.782 e Å^{-3}

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

*Complex **1***			
Cd(1)–N(6)#1	2.309(4)	Cd(1)–Cl(2)	2.7342(14)
Cd(1)–N(3)	2.331(4)	Cd(2)–N(2)#2	2.439(4)
Cd(1)–O(1)	2.351(4)	Cd(2)–Cl(2)	2.5396(12)
Cd(1)–N(1)	2.388(4)	Cd(2)–Cl(1)	2.6893(14)
Cd(1)–Cl(1)	2.5681(13)		
N(6)#1–Cd(1)–N(3)	108.06(14)		
N(6)#1–Cd(1)–O(1)	84.61(13)	N(1)–Cd(1)–Cl(2)	96.48(10)
N(3)–Cd(1)–O(1)	89.49(13)		
N(6)#1–Cd(1)–N(1)	165.62(14)	N(2)#2–Cd(2)–Cl(2)	90.88(10)
N(3)–Cd(1)–N(1)	71.88(13)	N(2)#3–Cd(2)–Cl(2)	89.12(10)
O(1)–Cd(1)–N(1)	81.02(13)		
N(6)#1–Cd(1)–Cl(1)	92.49(11)	N(2)#2–Cd(2)–Cl(1)	88.60(11)
N(3)–Cd(1)–Cl(1)	156.98(10)	N(2)#3–Cd(2)–Cl(1)	91.40(11)
O(1)–Cd(1)–Cl(1)	103.00(10)	Cl(2)#4–Cd(2)–Cl(1)	93.34(4)
N(1)–Cd(1)–Cl(1)	90.82(10)	Cl(2)–Cd(2)–Cl(1)	86.66(4)
N(3)–Cd(1)–Cl(2)	81.97(10)	Cl(1)–Cd(1)–Cl(2)	85.15(4)
O(1)–Cd(1)–Cl(2)	171.45(9)	N(6)#1–Cd(1)–Cl(2)	97.74(10)
*Complex **2***			
Cd(1)–N(2)#1	2.330(3)	Cd(1)–N(3)	2.465(2)
Cd(1)–N(1)	2.410(3)		
N(2)#1–Cd(1)–N(2)#2	83.85(14)	N(1)#3–Cd(1)–N(3)	82.69(9)
N(2)#1–Cd(1)–N(1)	96.08(10)	N(1)–Cd(1)–N(3)	70.38(9)
N(2)#2–Cd(1)–N(1)	167.51(10)	N(2)#2–Cd(1)–N(3)	97.82(9)
N(1)#3–Cd(1)–N(1)	86.67(13)	N(3)–Cd(1)–N(3)#3	142.88(12)
N(2)#1–Cd(1)–N(3)	109.73(9)	N(4)–N(2)–Cd(1)#4	116.53(19)

Symmetry codes: #1 = $-x+1$, $-y+1$, $-z$; #2 = $-x$, $-y$, $-z+1$; #3 = $x+1$, $y+1$, z; #4 = $-x+1$, $-y+1$, $-z+1$; #5 = $x-1$, $y-1$, z for **1**. #1 = $-x+1/2$, $y-1/2$, $-z+1/2$; #2 = $x+1/2$, $y-1/2$, z; #3 = $-x+1$, y, $-z+1/2$; #4 = $x-1/2$, $y+1/2$, z for **2**.

$\omega - 2\theta$ scan mode at 296(2) K. The data integration and reduction were processed with SAINT software. The structures were solved by direct methods with SHELXS-97 [21]. The hydrogens were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical constraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [22]. Table 1 shows crystallographic and refinement data for **1** and **2**. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of crystal structures*

3.1.1. Crystal structure of $[Cd_{1.5}(L)Cl_2(H_2O)]_{2n}$ (1). Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the P-1 space group and exhibits a layered 2-D framework. The asymmetric unit consists of one and a half Cd(II) ions, one L^-, and two coordinated chlorides. One crystallographically independent Cd(II), Cd1, possesses a distorted octahedral coordination geometry with three nitrogens of two different L, two chlorides and one oxygen of coordinated water. The other Cd(II), Cd2, is located on an inversion center and is coordinated by a nitrogen from two different L^- and four chlorides. A linear trinuclear Cd(II) cluster arises *via* the inversion center with the two crystallographically equivalent Cd1 and Cd1A ions in terminal positions and one Cd2 in the center

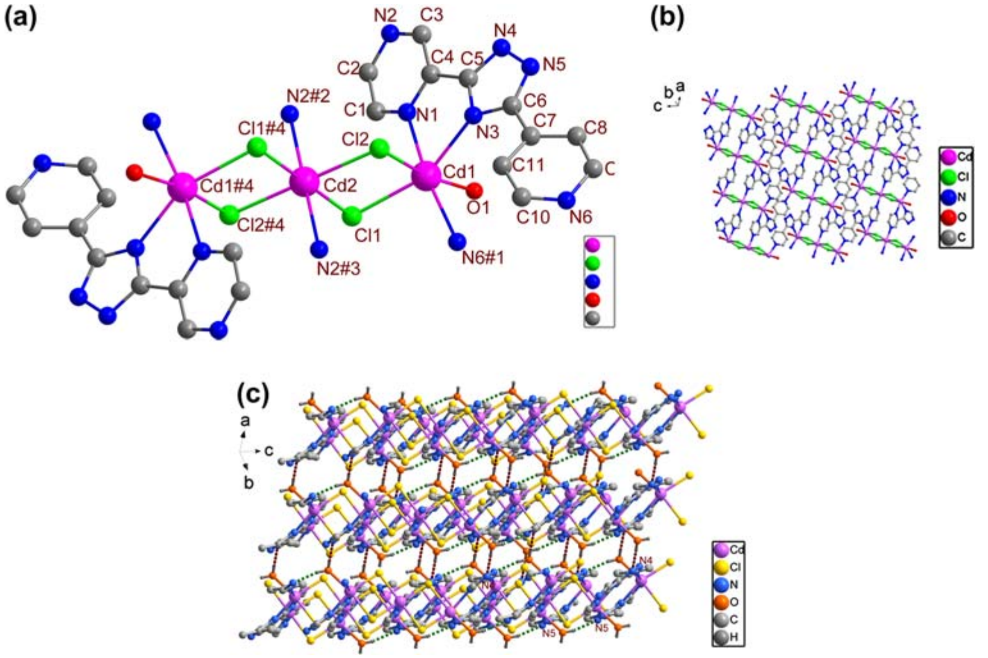

Figure 1. Views of **1**: (a) The coordination environment of Cd(II) (symmetry codes: #1 $-x+1$, $-y+1$, $-z$; #2 $-x$, $-y$, $-z+1$; #3 $x+1$, $y+1$, z; #4 $-x+1$, $-y+1$, $-z+1$). (b) The 2-D network of **1**. (c) A view of the 3-D supramolecular framework of **1** *via* O1–H1C···N4 (red) and O1–H1B···N5 (green) interactions.

(figure 1(a)). Cd1 and Cd2 are bridged by two chlorides and the Cd–Cd distance is 3.847 Å. The Cd1−N distances are 2.309(4)−2.388(4) Å. The Cd1−O1 distance is 2.351(4) Å. The octahedron of Cd2 is compressed along the N2−Cd2−N2′ axis, as shown by the distances Cd(2)−N(2) 2.439(4) Å, Cd(2)−Cl(1) 2.6893(14) Å, and Cd(2)−Cl(2)) 2.5396(12) Å. The chlorides are μ_2-bridges and Cd−Cl distances are 2.5396(12)−2.7342(14) Å. The Cd1−Cl1−Cd2 and Cd1−Cl2−Cd2 angles are 94.04(4)° and 93.61(4)°, respectively. These bond angles and distances fall in the normal range [23–25]. The repeating trinuclear subunits are linked by two L^- into a 2-D layered network (figure 1(b)). These 2-D layers are further assembled into a 3-D supramolecular framework through O–H···N hydrogen-bonding interactions (O1–H1B···N5 = 2.811(6) Å, 164(7)°; O1–H1C···N4 = 2.837(6) Å, 178(7)°) (red and green dashed lines in figure 1(c)).

3.1.2. Crystal structure of $[CdL_2]_n$ (2).

Single-crystal X-ray diffraction (XRD) indicates that **2** has a 2-D layered structure, the asymmetric unit of which consists of one Cd

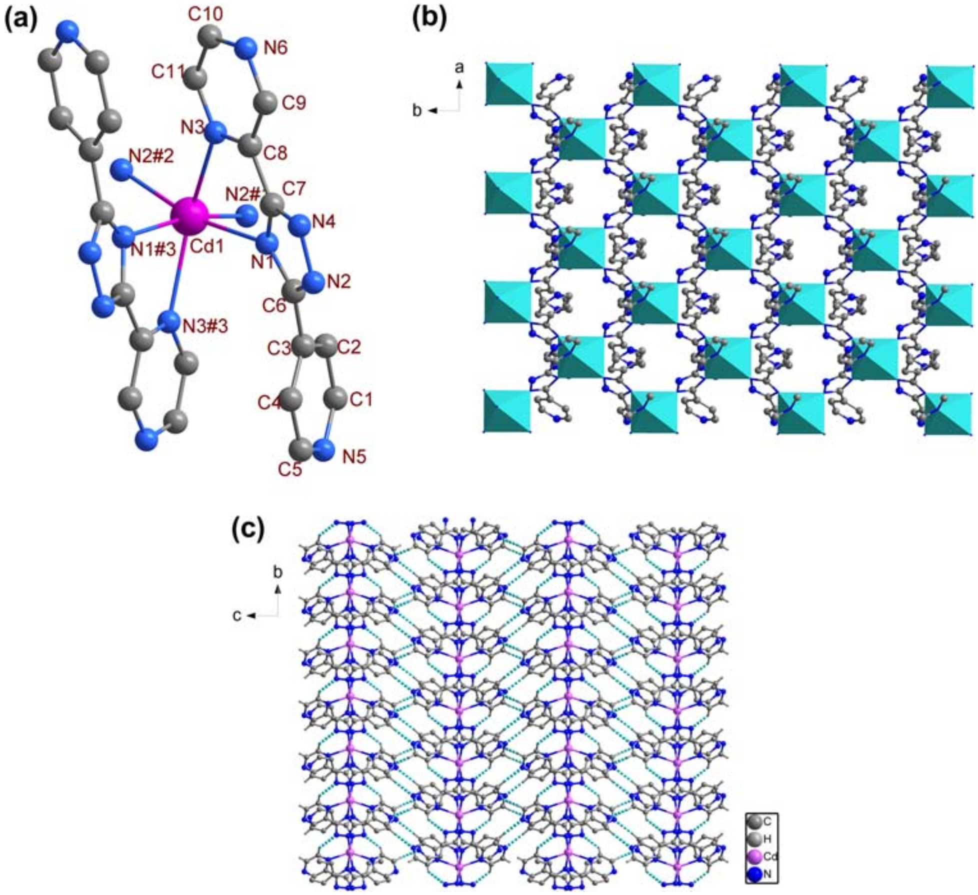

Figure 2. Views of **2**: (a) The coordination environment of Cd(II) (symmetry codes: #1 −*x* + 1/2, *y* − 1/2, −*z* + 1/2; #2 *x* + 1/2, *y* − 1/2, *z*; #3 −*x* + 1, *y*, −*z* + 1/2). (b) Perspective view of the 2-D coordination layer. (c) A view of the 3-D supramolecular framework of **2**.

and two L$^-$. Cd(II) is located in a six-coordinate environment (figure 2(a)), surrounded by six nitrogens, four coming from the chelating pyrazine–triazole segment of two L$^-$ and two more from two other, symmetry-related triazole rings. The Cd–N bond length varies from 2.330(3) to 2.465(2) Å and the N−Cd−N angles are 82.69(9)°−109.73(9)°. These values are in the normal range observed in related compounds [26,15]. Each L$^-$ links two Cd(II) ions and in turn each Cd(II) connects to four L$^-$ linkers, forming a layered structure with (4, 4) grid units. All Cd(II) ions are located in one plane (figure 2(b)), with Cd···Cd distances of 6.887 and 8.267 Å. These 2-D layers are further combined to form a 3-D coordination framework by weak C−H···N hydrogen bonds between nitrogen from L$^-$ and H−C from pyrazine and pyridine rings (C···N 3.220(4)–3.512(5) Å and C–H···N 140–175°) (figure 2(c)).

3.2. *Hydrothermal synthesis*

Because mixing metal salts and multidentate ligands containing N-donor substituents usually results in precipitation in traditional aqueous reactions, hydrothermal methods were adopted in our studies and are a powerful approach for the preparation of functional organic-inorganic hybrid materials [27,28]. Similar to the synthesis of **1** and **2**, Li *et al.* [19] obtained a hexagonal porous coordination architecture $[Cu(L)_2]_n$ under solvothermal conditions at 160 °C, but this compound reverted to the molecular species $[Cu(L)_2(H_2O)]$ when exposed to water vapor. Chen *et al.* [20] obtained a mononuclear compound $[Zn(L)_2(H_2O)_2]$ by room temperature evaporation. Different reaction conditions thus produce structures of different dimensions. High temperature may be beneficial to obtain high dimension structures, and room temperature may tend to obtain mononuclear structures. However, further studies are still required to better understand the reason for formation of different types of structures.

3.3. *Thermal stability of 1 and 2*

Coordination polymers **1** and **2** are stable at ambient conditions and TG analyzes were performed to explore their thermal stability (Supplementary Material). **1** gives a gradual weight loss of 3.73% from 254 to 344 °C, which corresponds to loss of coordinated water (calculated 3.75%). The second weight loss at 468–520 °C (14.35%) is in agreement with the calculated value (14.75%) for loss of chlorine. The remainder decomposed continuously until the heating ended at 900 °C. The TG curve of **2** showed that it was stable to 480 °C. At 480–540 °C, a sharp weight loss process is ascribed to loss of pyridine rings from two L$^-$ (exptl: 26.53%, Calcd: 27.94%). Continuous weight loss from 540 to 900 °C resulted from the decomposition of residual ligand skeleton. These results indicate that the complexes are thermally stable for further applications.

3.4. *Fluorescence of 1 and 2*

Photoluminescence of **1**, **2**, and HL were studied in the solid state at room temperature; emission spectra are shown in Supplementary Material. Blue emission for **1**, **2**, and HL can be observed, where the maximum emission wavelength is at 389 nm (under 280 nm excitation) for HL, 447 nm (under 320 nm excitation) for **1**, and 409 nm (under 280 nm excitation) for **2**. Compared with the emission spectrum of HL, a red shift of 58 nm and lower intensity for **1** suggest that luminescence of the ligand is remarkably affected by metal centers, providing electronic interactions between the transition metal and the ligand framework and contributing to the delocalized π-electron system. The red shift of 20 nm with higher intensity for **2** is the result of ligand to metal charge transfer [29]; considerable enhancement of the emission intensity for **2** compared with free HL may result from increased rigidity of the organic ligand when binding to Cd(II), which will effectively reduce the loss of energy [30,31].

3.5. *Powder XRD of 1 and 2*

To confirm the phase purity of the bulk materials, X-ray power diffraction experiments were carried out on **1** and **2**. The powder XRD pattern and simulated XRD pattern of **1** and **2** are depicted in Supplementary Material. The measured powder XRD pattern is in agreement with the simulated pattern by X-ray single crystal data, indicating phase purities of the samples. The difference in reflection intensities between simulated and experimental patterns is due to different orientations of the crystals in the powder samples.

4. Conclusion

Two new polymers have been obtained by hydrothermal reactions of cadmium salts with HL, 3-(pyridin-4-yl)-5-(pyrazin-2-yl)-1H-1,2,4-triazole. Complexes **1** and **2** are both 2-D layer structures which expand to 3-D supramolecular architectures *via* hydrogen bonding. Fluorescence of HL, **1** and **2** have been studied in the solid state at room temperature. Complex **2** displayed strong fluorescent emission bands at 409 nm upon excitation at 280 nm at room temperature. This approach may be useful for construction of a variety of new transition metal complexes and luminescent coordination polymers that have potential for new fluorescent materials.

Supplementary material

X-ray crystallographic files in CIF format for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC Nos. 886584 and 886585. The data can be freely obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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