SHORT PAPER

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An extended network *via* hydrogen bond linkage of the linear coordination polymer $[Cd(\mu\text{-dptz})(NO_3)_2]_\infty$[†]

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The crystal structure of $[Cd(\mu\text{-dptz})(NO_3)_2]_\infty$ reveals a neutral one-dimensional coordination polymer exhibiting a two-dimensional architecture through inter-chain hydrogen-bonding.

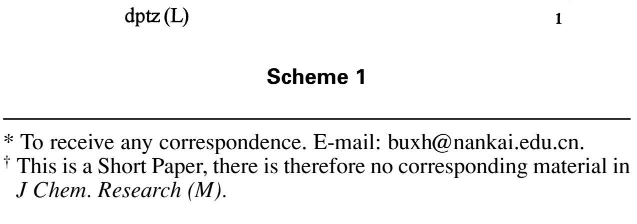
Keywords: hydrogen bonding, $[Cd(\mu\text{-dptz})(NO_3)_2]_\infty$

Self-assembly processes directed by either hydrogen bonding or metal coordination have been extensively utilised to construct supramolecular systems with novel topology and potential optical, electronic and magnetic functions, as well as intercalation systems for ion- or molecule-exchange and catalytic properties.[1–5] The strategies for the construction of functional systems depend on the nature of the interactions responsible for creating networks. One of the best strategies to fabricate two-dimensional (2-D) and three-dimensional (3-D) systems is to utilise the hydrogen bonding of the coordinated ligands in addition to their coordination capability. Although a useful way to realise this strategy is to interlink the one-dimensional (1-D) coordination polymers *via* the hydrogen-bonding interactions between the chains, networks assembled in this way are relatively rare.[6]

3,6-Di-2-pyridyl-1,2,4,5-tetrazine (dptz), a well known functional ligand, has been extensively investigated as a coordinative π-acceptor moiety of transition metal complexes.[7] Focusing the interest on polynuclear systems, dptz has been used as a bridging ligand to construct molecular square or pentagon complexes,[8] and independently we have shown an interesting chiral molecular box of dptz, $[Zn_4(dptz)_4(H_2O)_4(CH_3CN)_4]$[8a],[9] In a systematic work aimed at the construction of polymeric complexes of dptz, we report herein a 1-D linear complex $[Cd(\mu\text{-dptz})(NO_3)_2]_\infty$ which exhibits an extended 2-D network *via* hydrogen bonding between adjacent chains.

Reaction of $Cd(NO_3)_2{\cdot}2H_2O$ with dptz afforded red crystals of the title complex (Scheme 1). The IR spectrum of **1** displays a very strong and sharp characteristic band at 1394 cm^{-1} and a peak at 816 cm^{-1}, indicating the presence of the NO_3^- anions. The peaks in the range 1200–1600 cm^{-1} are attributed to the skeletal vibrations of the aromatic rings.

The crystal structure of **1** reveals that dptz forms a one-dimensional linear structure with Cd^{II} as shown in Fig. 1. Each Cd^{II} centre in this chain has a typical octahedral coordination geometry due to the high symmetry. The Cd^{II} ion is bridged by a dptz ligand in the *trans*-conformation [Cd-N = 2.325(3), 2.448(3) Å] to give a 1:1 ligand/metal infinite polymeric chain. The coordination sphere at Cd^{II} is completed by two oxygen donors of two nitrate anions [Cd–O = 2.338(3) Å], and therefore a neutral Cd^{II} coordination polymer is formed. The intra-chain adjacent Cd···Cd separation is 7.559(4) Å and the shortest inter-chain distance is 7.868(3) Å. Comparing this structure with $[Zn_4(dptz)_4(H_2O)_4(CH_3CN)_4]$[8a],[9] we find that dptz bridges the metal centres in different arrangements: the neighbouring dptz molecules are vertical in the Zn^{II} complex, whereas they are parallel when coordinated to Cd^{II}. It seems that the presence of the nitrate anion as opposed to perchlorate and/or the differences of the ion radius between Zn^{II} and Cd^{II} have made the structure of this compound so different from that of Zn^{II}.[9]



Scheme 1

The most striking feature of this complex resides in its structure to form an extended 2-D network through C(14)–H(14)···O(2)[i] (*i* = *x*,*y*,*z*–1) interaction. The H atom from the pyridine ring has been activated by the positive charge due to the coordination of N atoms to the Cd^{II} centre. Each nitrate anion in the neighbouring chain forms the acceptor in a hydrogen bond to give this extended network as depicted in Fig. 2. The C···O separation is 3.201 Å with H···O length 2.526 Å, falling into the range of 3.0–4.0 Å for C···O separation suggested by Desiraju,[10] and the bond angle is 129.7°. In addition, the separation of the parallel dptz molecules is 3.777 Å, indicating weak π-π interactions which stablise the 2-D network structure.

In conclusion, complex **1** is a nice example to construct a 2-D system by interlinking the 1-D coordination polymer *via* the hydrogen bonds between the chains, which also enriches the coordination chemistry of dptz.

Experimental

Elemental analyses were performed on a Perkin-Elmer 240C analyzer and IR spectra were measured on a FT-IR 170SX (Nicolet) spectrometer in KBr pellets. All reagents and solvents for syntheses and analyses were of analytical grade.

Preparation of **1**: To a solution of $Cd(NO_3)_2{\cdot}2H_2O$ (0.2 mmol) in CH_3CN (15 ml) was added a solution of dptz (0.2 mmol) in $CHCl_3$ (10 ml) to give a red solution. After stirring for 30 min the solution was filtered. Red single crystals suitable for structure determination were obtained by slow evaporation of the solvent in 75% yield. Anal. Calcd for $C_{12}H_8CdN_8O_6$: C, 30.49; H, 1.71; N, 23.71. Found: C, 30.22; H, 1.99; N, 23.44. IR (KBr pellet, cm^{-1}): 1597*m*, 1448*s*, 1394*vs*, 1306*s*, 1258*w*, 1090*m*, 1016*m*, 816*m*.

X-ray analysis: Single crystal X-ray diffraction measurement was carried out with a Simens CCD X-ray diffractometer with MoKα radiation (λ = 0.71073 Å) at 193(2) K. The structure was solved by direct methods and using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

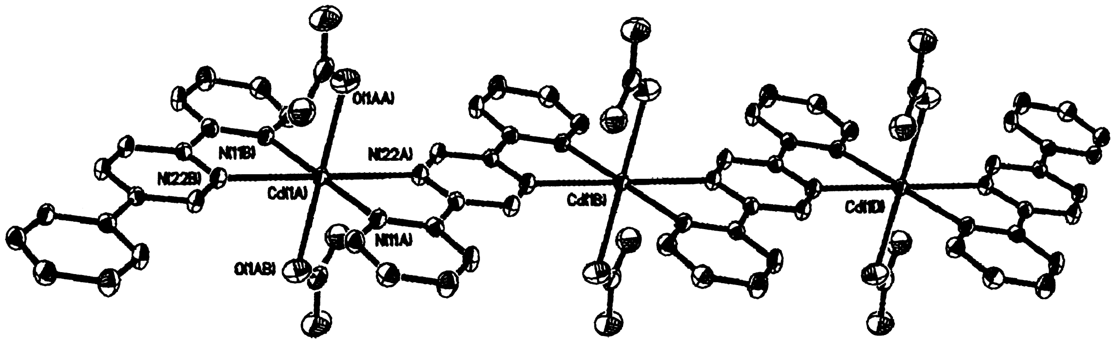

Fig. 1 ORTEP view of the neutral coordination chain 1 with 50% thermal ellipsoids.

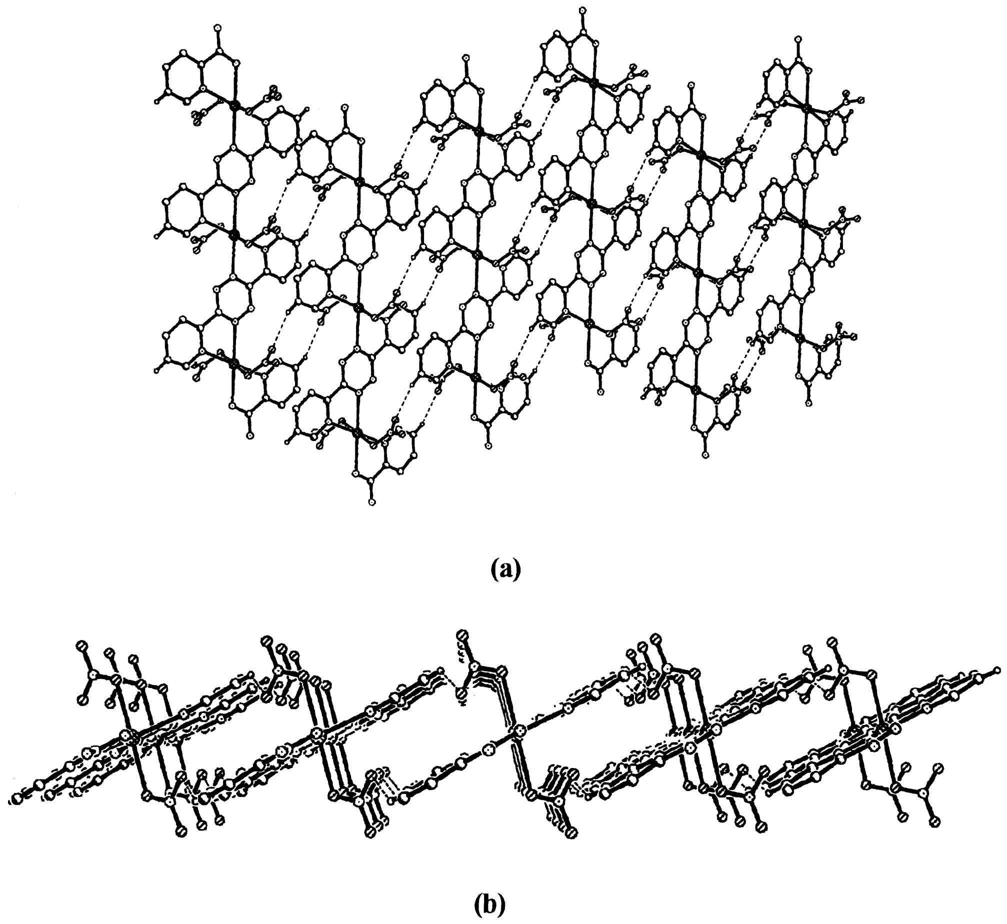

Fig. 2 A view of the extended network of **1** along (a) (1 0 1) plane, (b) (0 1 1) plane.

calculated positions and thereafter allowed to ride on their parent atoms. Crystal data for **1**: $C_{12}H_8CdN_8O_6$, $Mr = 472.66$, triclinic, space group $P\text{–}1$, $a = 7.5594(8)$, $b = 7.8682(10)$, $c = 8.1125(10)$ Å, $\alpha = 65.947(4)°$, $\beta = 67{,}323(4)°$, $\gamma = 63.138(4)°$, $V = 380.88(8)$ Å^3, $Z = 1$, $Dc = 2.061$ g/cm^3, μ (Mo–Kα) = 1.490 mm^{-1}, $F(000) = 232$. A total of 3296 reflections were collected and the independent reflection number is 1820 with 124 refined parameters ($R_{\text{int}} = 0.0443$). Final convergent [$I \geq 2\sigma(I)$] $R = 0.0394$, $wR = 0.0763$ and Goodness-of-fit = 0.964. Full crystallographic details will be deposited at the Cambridge Crystallographic data Center (CCDC).

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