# One-dimensional Coordinate Polymer involving Heptacoordinate Cadmium(II) Ions

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A one-dimensional polymer $\{[Cd_2(\mu\text{-bpe})_3](NO_3)_4\}_n$ [**1**, bpe = 1,2-bis(4-pyridyl)ethane] is prepared; its structure is strikingly characterised by heptacoordinate $Cd^{II}$ ions as well as by a unique main framework, *i.e.* two bpe units bridge two $Cd^{II}$ ions giving a cyclic closed structure which is linked to the next one by another bpe unit.

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In search of molecular-based materials with such functions as catalysis,[1] magnetism[2] and clathration,[1,3] coordinate polymers of one-,[4] two-,[1,2,5,6] and three-dimensional[5,7] infinite frameworks have been extensively studied recently. Although rigid bridged ligands were frequently employed to construct these materials, flexible ligands were exploited less for this purpose. We report here the preparation and structure determination of a one-dimensional coordinate polymer, $\{[Cd_2(\mu\text{-bpe})_3](NO_3)_4\}_n$ **1**, [bpe = 1,2-bis(4-pyridyl)ethane], in which flexible bpe molecules link $Cd^{II}$ ions in two different patterns, making a one-dimensional array of $Cd^{II}$ and bpe in a 2:3 stoichiometry. In addition to the unique one-dimensional alignment, a more striking structural feature of this complex is that the $Cd^{II}$ ion has uncommon heptacoordinate geometry.[8]

Polymer **1** was easily prepared from $Cd(NO_3)_2$ and bpe. An ethanol solution of bpe (0.2 mol $dm^{-3}$, 0.4 $cm^3$) was combined with an aqueous solution of $Cd(NO_3)_2$ (0.1 mol $dm^{-3}$, 1.6 $cm^3$) and the mixture was allowed to stand for 3 d at room temp. giving **1** as colourless crystals in 39% isolated yield. Elemental analysis agreed with the formula of **1**. Other crystals of different crystal packing or compositions were not formed even if the ratio of $Cd(NO_3)_2$ to bpe before crystallization varied in a range of 1:1 to 1:4.

The one-dimensional infinite structure of **1** was shown by an X-ray diffraction study† (Fig. 1). Two bpe units bridge two $Cd^{II}$ atoms, giving a cyclic closed structure which is linked to the next one by another bpe unit. The crystal packing of **1** is interesting, *i.e.* the one-dimensional polymers align parallel with each other to make a molecular sheet stacked orthogonally on the next sheet with interplanar separation of 4.76 Å.

From a structural standpoint, the one-dimensional polymer **1** is characterized by heptaccoordinate $Cd^{II}$ ions (Fig. 2).[8] The geometry can be regarded as distorted pentagonal bipyramidal with two nitrate ions and a pyridyl group at the equatorial positions and two pyridyl groups at the apical positions. Coordinating oxygen and nitrogen atoms at the equatorial positions are almost coplanar, but the alignment of the two apical pyridyl groups is somewhat deviated from 180° (N(2)–Cd(1)–N(3) 172.90°). The heptacoordination of the $Cd^{II}$ ion is shown by the following. First, two oxygen atoms of each nitrate ion coordinate with $Cd^{II}$ ion almost equally, and the Cd–O distances (2.41–2.49 Å) are quite similar to normal $Cd^{II}\text{–}ONO_2$ distances (2.49 Å).[1] Secondly, other Cd–N(pyridyl) bonds (2.32–2.34 Å) also have typical bond lengths (2.36–2.37 Å).[1] Thirdly, the coordination of each atom is not forced by the geometry of other coordinating atoms, though there are many examples of apparent seven coordination forced by geometrical demands of polydentate ligands.[8]

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics, No. 06227214, from the Ministry of Education, Science and Culture, Japan.

*Received, 24th May 1994; Com. 4/03112A*

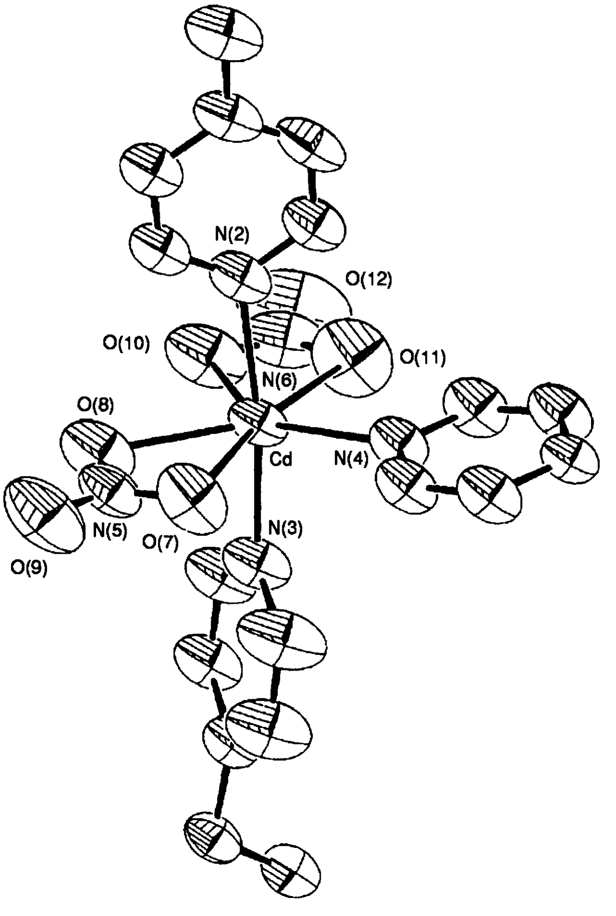

**Fig. 2** ORTEP drawing of the environment of $Cd^{II}$ ion. Selected bond distances (Å) and angles (°) are as follows: Cd(1)–O(7) 2.479, Cd(1)–O(8) 2.422, Cd(1)–O(10) 2.413, Cd(1)–O(11) 2.457, Cd(1)–N(2) 2.340, Cd(1)–N(3) 2.315, Cd(1)–N(4) 2.334, O(7)–Cd(1)–N(4) 84.48, O(11)–Cd(1)–N(4) 85.16, O(8)–Cd(1)–O(10) 86.67, O(10)–Cd(1)–O(11) 52.09, N(2)–Cd(1)–N(3) 172.90.

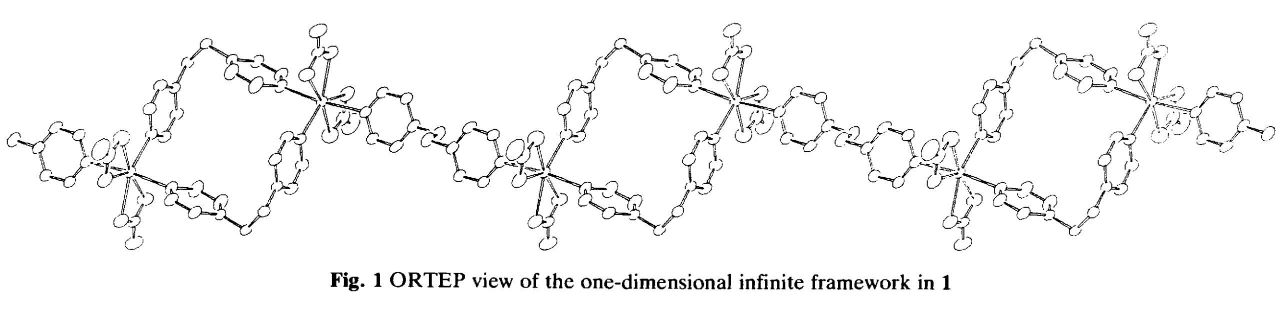

**Fig. 1** ORTEP view of the one-dimensional infinite framework in **1**

## Footnote

† *Crystal data* for **1**: monoclinic, *P*21/*n*, $a = 12.529(4)$, $b = 17.185(5)$, $c = 9.530(3)$ Å, $\beta = 92.49(2)°$, $V = 2050(1)$ Å$^3$, $Z = 4$, $D = 1.66$ g cm$^{-3}$, $F(000) = 1027$, $\lambda$(Mo-K$\alpha$) = 0.71073 Å, 5326 reflections measured, 3717 observed [$F > 3.00\ \sigma(F)$], number of parameters 311, $R = 0.0342$; $R_w = 0.0359$. Atomic coordinates bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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