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catena-Poly[[dichloridomercury(II)]-μ-1-(2-pyridylmethyl)-1*H*-benzotriazole]: the effect of different metal centers on the self-assembly of coordination complexes

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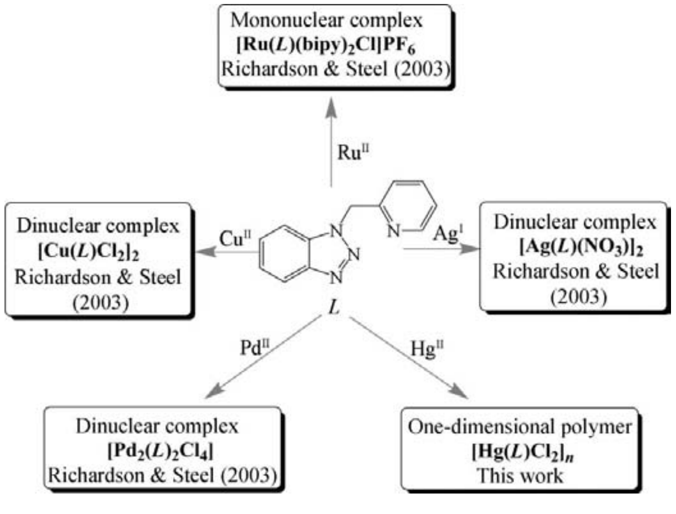
To further investigate the relationship between the structures of benzotriazol-1-yl-based pyridyl ligands and their complexes, a new linear one-dimensional Hg^{II} coordination polymer, $[HgCl_2(C_{12}H_{10}N_4)]_n$, with the 1-(2-pyridylmethyl)-1*H*-benzotriazole (*L*) ligand was obtained through the reaction of *L* with $HgCl_2$. In this complex, each Hg^{II} center within the one-dimensional chain is coordinated by two chloride anions as well as by one pyridine and one benzotriazole N-atom donor of two distinct *L* ligands in a distorted tetrahedral geometry, forming a linear one-dimensional chain running along the [010] direction. Weak C—H$\cdots\pi$ and π–π stacking interactions link the one-dimensional motifs to generate an overall two-dimensional network parallel to the (100) plane. Comparison of the structural differences with previous findings suggests that the presence of different metal centers may plays an important role in the construction of such supramolecular frameworks.

Comment

In recent years, increasing attention has been focused on the construction of coordination polymers, also known as metal–organic frameworks (Janiak, 2003; Robin & Fromm, 2006). The rational engineering and controlled preparation of such novel coordination polymers are currently of great interest in coordination and supramolecular chemistry because of their interesting topologies (Chen *et al.*, 2006; Hill *et al.*, 2005; Kitagawa *et al.*, 2004; Liu, Chang *et al.*, 2008; Steel, 2005; Wang *et al.*, 2008; Yaghi *et al.*, 2003) and potential uses as functional materials (Bu *et al.*, 2004; Hou *et al.*, 2005; Liu, Sañudo *et al.*, 2008; Liu *et al.*, 2007; Tao *et al.*, 2008). One of the most successful strategies for constructing such complexes has been the assembly reaction of different metal ions (as nodes) with well designed organic ligands (as building blocks), which, so far, has been at an evolutionary stage with the current focus mainly on understanding the factors that determine the crystal packing, as well as exploring relevant potential properties (Chen *et al.*, 2006; Du *et al.*, 2007; Liu *et al.*, 2006; Zou *et al.*, 2006). In addition, various intra- and/or inter-molecular weak interactions, such as π–π stacking (Janiak, 2000) and C—H$\cdots\pi$ (Sony & Ponnuswamy, 2006) and C—H$\cdots X$ (X = O, N, S, F, Cl, Br, I, and so on) hydrogen-bonding (Desiraju & Steiner, 1999) interactions, also affect the final structures of coordination complexes, especially in the aspect of linking multinuclear discrete subunits or low-dimensional motifs into higher-dimensional frameworks.

Numerous related bis-heterocyclic chelating or bridging ligands have been synthesized and have been used extensively to construct functional coordination complexes that contain different hetero-aromatic ring systems, for example, pyridine, pyrazine, quinoline, quinoxaline, pyrazole, imidazole, thiazoles and their benzo analogues (Constable, 1989; Constable & Steel, 1989; Steel, 2005). Richardson & Steel (2003) have reported studies concerning five N-containing bis-heterocyclic ligands bearing 1-substituted benzotriazole subunits (see the first scheme below). In our previous work, we have also reported the preparation of a nonplanar flexible benzotriazol-1-yl-based pyridyl ligand, namely 1-(4-pyridylmethyl)-1*H*-benzotriazole (4pbt). Its reaction with $AgNO_3$ led to a one-dimensional double-helical coordination polymer, $\{[Ag(4pbt)]NO_3\}_n$, formed by C–H$\cdots\pi$ supramolecular interactions between adjacent single-helical chains (Liu, Sun *et al.*, 2008). The results therein indicated that the N-donor spatial position of the pendant pyridyl group in such benzotriazol-1-yl-based pyridyl ligands, as compared with the previous findings (Richardson & Steel, 2003), played an important role in determining the final structures of relevant coordination complexes.



As part of a study on the coordination possibilities of benzotriazole-based ligands with different metal centers in the self-assembly process of coordination complexes, we have

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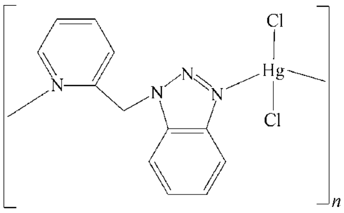
chosen sequentially the ligand 1-(2-pyridylmethyl)-1*H*-benzotriazole (*L*) to construct a new one-dimensional Hg^{II} complex though its reaction with $HgCl_2$ under a conventional solution method. We report here the crystal structure of $[Hg(L)Cl_2]_n$, (I), and briefly discuss the effect of the coordination geometry of different metal centers on the structures of the relevant coordination complexes.



(I)

The crystal structure of (I) consists of one-dimensional linear neutral $[Hg(L)Cl_2]_n$ chains (Fig. 1). In each one-dimensional chain, there exists only one type of crystallographically independent Hg^{II} center, which is four-coordinated by two chloride anions and two N-atom donors, one from the benzotriazole ring of one *L* ligand and the other from the pyridine ring of another distinct *L* ligand. The Hg—N and Hg—Cl bond distances, as well as the bond angles around each Hg^{II} center (Table 1), are within the expected range for such complexes (Orpen *et al.*, 1989; Wang *et al.*, 2007). The coordination geometry around the Hg^{II} center can be described as a distorted tetrahedron. Each *L* ligand takes a μ_2-bridging coordination mode to connect the Hg^{II} centers, generating a perfect linear chain along the [010] direction, with adjacent Hg atoms separated by a *b*-axis translation [$Hg\cdots Hg = b = 8.8723\ (18)$ Å]. Moreover, adjacent one-dimensional chains are linked together to form an overall two-dimensional sheet running parallel to the (100) plane (Fig. 2) by the co-effects of interchain π–π stacking interactions between completely parallel benzotriazole rings of adjacent *L* ligands [the centroid–centroid separation is 3.706 (5) Å and the average interplanar separation is 3.4494 Å] (Janiak, 2000) and C—$H\cdots\pi$ supramolecular interactions involving the C7–C12 benzene rings of the *L* ligand (centroid *Cg*1, see Table 2) (Sony & Ponnuswamy, 2006). Thus, the various intra- or intermolecular weak interactions mentioned above play an important role in the formation of (I), especially in the aspect of linking the low-dimensional motifs into higher-dimensional supramolecular networks.

To explore the coordination possibilities of relevant benzotriazol-1-yl-based pyridyl bis-heterocyclic ligands, Richardson & Steel (2003) synthesized *L* and selected four different types of metal centers with different coordination geometries as representative subjects for coordination with it. A mononuclear complex, $[Ru(L)(bpy)_2Cl]PF_6$ (bpy is 2,2′-bipyridine), and a dinuclear complex, $[Pd_2(L)_2Cl_4]$, with an intramolecular Pd—Pd separation of 6.739 (1) Å, were obtained, while Ru^{II} and Pd^{II} were chosen as examples of stereoregular octahedral and square-planar metals to react with *L*. In addition, Cu^{II} (Melnik *et al.*, 2000) and Ag^{I} (Munakata *et al.*, 1998) centers have also proved very popular in recent years and have been widely employed as components for the construction of diverse coordination architectures with various N-containing heterocyclic ligands. For example, the previously reported metal–organic coordination architectures constructed from ligand *L* also include two centrosymmetric dinuclear complexes, $[Cu(L)]_2Cl_4$ and $[Ag(L)]_2(NO_3)_2$, where Cu^{II} and Ag^{I} were selected as examples of metals that have more flexible coordination numbers and geometries

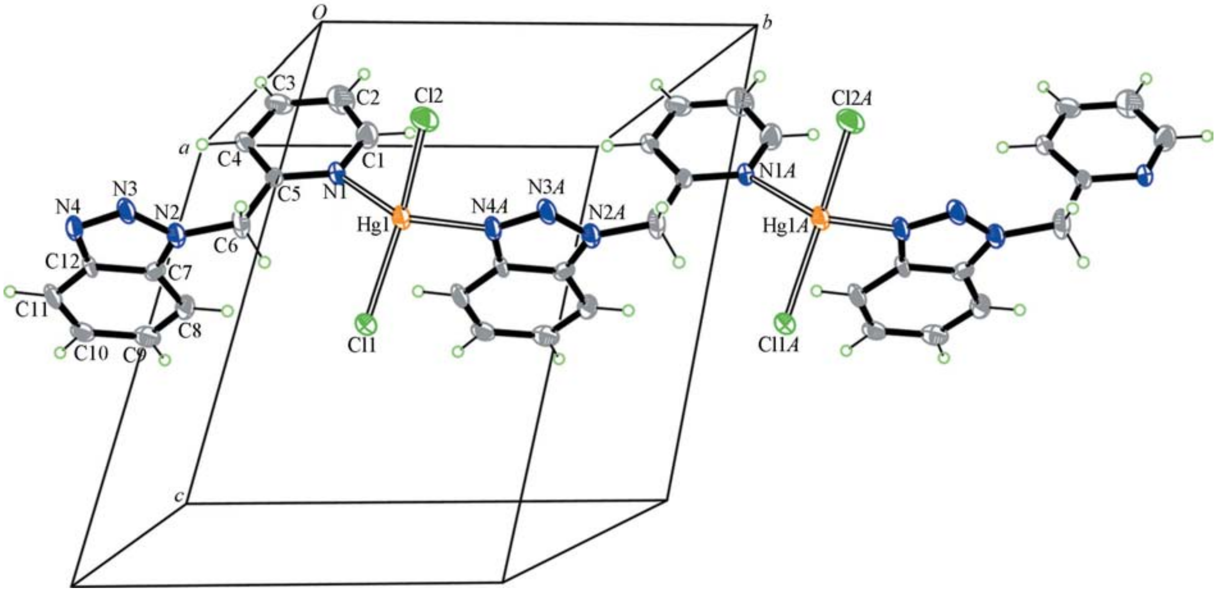


Figure 1
The one-dimensional molecular structure of (I), viewed along the *b* axis, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and atoms labeled with the suffix *A* are generated by the symmetry operation (x, $y + 1$, z).

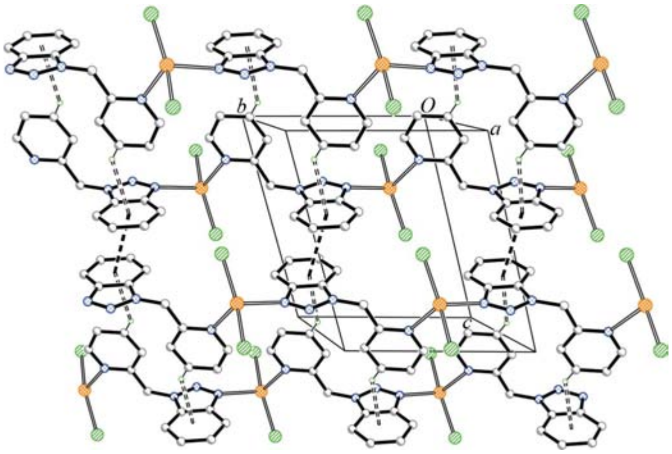


Figure 2
The two-dimensional network, running parallel to the (100) plane, formed by interchain π–π stacking (solid dashed lines) and C—H$\cdots\pi$ (open dashed lines) interactions. For clarity, only H atoms involved in these interactions are shown.

(Richardson & Steel, 2003). In this contribution, when we used $HgCl_2$ to react with *L* under conventional solution conditions, a perfect one-dimensional linear coordination polymer, $[Hg(L)Cl_2]_n$, (I), was produced, in which the coordination geometry around the Hg^{II} center can be described as a distorted tetrahedron. Thus, in comparison with the previous finding, the present work reveals that the coordination geometry of different metal centers could play an important role on the final structures of relevant coordination complexes. This fact may offer the means to construct coordination architectures with potentially useful properties just by variation of the metal center.

Experimental

The ligand *L* was synthesized according to the method reported by Liu, Sun *et al.* (2008). A solution of $HgCl_2$ (0.1 mmol) in a mixture of CH_3OH (15 ml) and CH_3CN (5 ml) was added to *L* (0.1 mmol). The yellow solid that formed was filtered off and the resulting solution was kept at room temperature. Yellow single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of the solvent after several days (yield ~40%). Elemental analysis calculated for $C_{12}H_{10}Cl_2HgN_4$: C 29.92, H 2.09, N 11.63%; found: C 29.81, H 2.17, N 11.51%.

Crystal data

$[HgCl_2(C_{12}H_{10}N_4)]$
M_r = 481.73
Triclinic, $P\bar{1}$
a = 7.8769 (16) Å
b = 8.8723 (18) Å
c = 11.130 (2) Å
α = 102.88 (3)°
β = 98.22 (3)°
γ = 109.70 (3)°
V = 693.4 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 11.47 mm^{-1}
T = 293 (2) K
0.19 × 0.17 × 0.12 mm

Data collection

Bruker *P*4 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.131, T_{max} = 0.257
6923 measured reflections
2444 independent reflections
2190 reflections with $I > 2\sigma(I)$
R_{int} = 0.081

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.120
S = 1.11
2444 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.13 e Å^{-3}
$\Delta\rho_{min}$ = −1.85 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—Cl2	2.329 (3)	Hg1—N4^i	2.460 (9)
Hg1—Cl1	2.348 (3)	Hg1—N1	2.548 (9)
Cl2—Hg1—Cl1	155.58 (13)	Cl2—Hg1—N1	97.1 (2)
Cl2—Hg1—N4^i	100.9 (2)	Cl1—Hg1—N1	98.4 (2)
Cl1—Hg1—N4^i	97.6 (2)	N4^i—Hg1—N1	91.1 (3)

Symmetry code: (i) $x, y+1, z$.

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C7–C12 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$\cdots$*Cg*1^{ii}	0.93	2.90	3.688 (3)	143

Symmetry code: (ii) $-x+2, -y, -z$.

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms [C—H = 0.93 (aromatic) or 0.97 Å (methylene), with U_{iso}(H) = 1.2U_{eq}(C)]. The position of the highest peak is at (0.4051, 0.7210, 0.1189), 1.43 Å from H2, and the position of the deepest hole is at (0.3568, 0.5704, 0.7213), 0.92 Å from Hg1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3087). Services for accessing these data are described at the back of the journal.

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