A Novel One-Dimensional Coordination Polymer Involving Weak Hg–Hg Interactions

by **Ali Morsali***[a]) and **Rhett Kempe**[b])

[a]) Department of Chemistry, School of Sciences, Tarbiat Modarres University, P. O. Box 14155-4838, Tehran, Iran (e-mail: morsali_a@yahoo.com)
[b]) Lehrstuhl Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth

The novel, stable, one-dimensional coordination polymer $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n\{(ClO_4)_4\}_n$ (**1**; dmap = 4-(dimethylamino)pyridine) has been synthesized and characterized. Single-crystal X-ray analysis showed that the coordination sphere of the two pertinent, zig-zag-oriented Hg^{II}-atoms is different. One type of Hg-atom in the $N_2O_4Hg{-}HgN_2O_4$ environment is seven-coordinate, with a weak Hg–Hg interaction. The other type of Hg^{II}-atom in the *trans*-HgN_2O_4 units is six-coordinate.

Introduction. – The design of crystal structures and the control of the molecular arrangement of coordination polymers has attracted much attention in recent years [1][2]. So far, extended systems of a variety of metals have been characterized, providing very interesting information about supramolecular isomerism. In most of these coordination polymers, spacer ligands such as 4,4′-bipyridine or 1,2-bis(pyridin-4-yl)ethane have been used [1][2]. Metallophilic Hg–Hg attractions in di- and hexametallic systems have been studied in recent years [3–7]. Nevertheless, the formation of coordination polymers with bridging metal ions such as Hg^{II} is relatively sparse, and coordination polymers involving Hg–Hg interactions have rarely been reported so far.

In the present paper, we report a novel structural motif based on bridging acetate and Hg–Hg moieties, giving rise to a one-dimensional coordination polymer.

Results and Discussion. – The reaction between 4-(dimethylamino)pyridine (dmap) and a 1:2 mixture of $Hg^{II}(OAc)_2$ and $NaClO_4$ provided crystalline materials of the general formula $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n\{(ClO_4)_4\}_n$ (**1**). X-Ray-diffraction analysis showed complex **1** to be a polymeric species arranged in a one-dimensional zig-zag chain (*Figs. 1* and *2*). The structure consists of discrete $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n^{4+}$ and ClO_4^- cations and anions, respectively, the former making up a zig-zag chain of Hg-atoms, involving interactions with both AcO^- and neighboring Hg-atoms (*Fig. 2,b*). The carboxylate moieties of the acetate ligands act as bidentate bridging groups in a μ-1,2 mode, where the acetate O(1)-atom bridges the two adjacent Hg^{2+} ions, in contrast to O(2), which is not coordinated to Hg.

In the structure of **1**, there are two Hg-atoms with fourfold coordination: HgO_2N_2 and $N_2OHg{-}HgN_2O$ units. Thereby, the environment of the two Hg-atoms is different. One is characterized by an array of O_2N_2 donor atoms, with distances of Hg(1)–N(1)

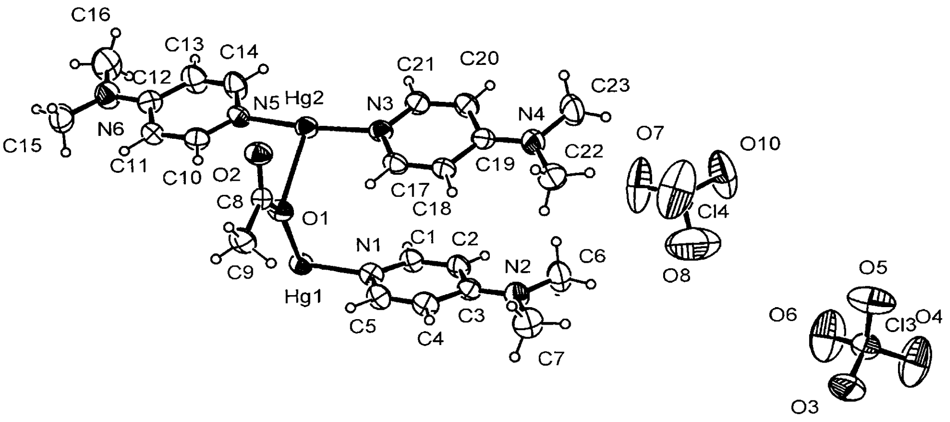

Fig. 1. *X-Ray single-crystal structure of the repeating unit in the complex* $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n[(ClO_4)_4]_n$ (**1**). dmap = 4-(dimethylamino)pyridine.

and Hg(1)−O(1) of 2.051(6) and 2.640(4) Å, respectively. The other Hg-atom is involved in an $N_2OHg-HgN_2O$ array, with distances of Hg(2)−N(3), Hg(2)−N(5), Hg(2)−O(1), and Hg(2)−Hg(2) of 2.070(6), 2.074(6), 2.508(4) and 3.4965(7) Å, respectively. The HgO_2N_2 units represent a regular square-planar coordination geometry, with an inversion center and D_{2h} symmetry. Each of these Hg-atoms is chelated by the pyridine N-atoms of two dmap ligands, as well as by two monodentate acetate anions, one acetate O-atom each forming a bridge between two Hg-atoms (*Fig. 2*). Thereby, the coordinating acetate O-atoms and the dmap N-atoms are in *trans* positions, the angles N(1)−Hg(1)−N(1) and O(1)−Hg(1)−O(1) being 180° (*Fig. 2,b*).

In the $N_2OHg-HgN_2O$ units, each Hg-atom is involved in a distorted tetrahedral geometry made up by two pyridine N-atoms from dmap, one O-atom of acetate, and one neighboring Hg-atom. The Hg−Hg distance is 3.4965(7) Å, which is smaller to the sum of their *Van der Waals* radii [3–5]. Hence, a weak metallophilic Hg−Hg interaction in **1** may be considered.

To find any potential donor center, it is necessary to extend the bonding limit to < 3.1 Å (sum of *Van der Waals* radii of Hg and O) [8]. Thus, the Hg(2)-atom is bonded to the acetate O(2)-atom, with distances Hg(2)−O(2) and Hg(2)−O(2)^{i} of 2.759 and 2.918 Å, respectively. Similarly, Hg(1) is bonded by a perchlorate O-atom, with distances of Hg(1)−O(2) and Hg(1)−O(5) of 2.719 and 2.986 Å (*Fig. 3*). Hence, the Hg^{II} coordination sphere is completed, and the coordination numbers for Hg(1) and Hg(2) are six (HgN_2O_4) and seven (HgN_2O_4Hg), respectively.

The carboxylate groups of the acetate anions act as bidentate as well as bridging groups (totally tetradentate). Thereby, the AcO^- groups are coordinated to one Hg-atom, and also bridge two adjacent Hg-atoms (*Fig. 4*).

The structure of $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n\{(ClO_4)_4\}_n$ (**1**) is further stabilized by typical intra-chain π/π stacking interactions [9] [10] between the dmap pyridine rings of adjacent units, the mean molecular planes being nearly parallel and separated by a distance of *ca.* 3.5 Å, resembling graphite planes. The parallel arrangement indicates that these interactions are of the 'stacking' rather than of the 'edge-to-face' or 'vertex-

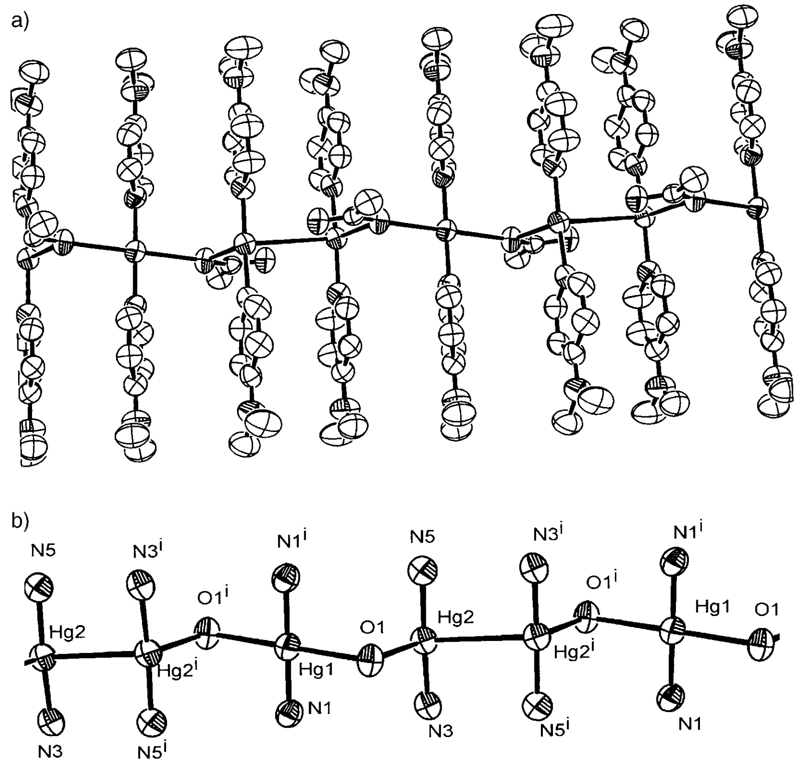

Fig. 2. *X-Ray crystal structure of* $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n[(ClO_4)_4]_n$ (**1**; dmap = 4-(dimethylamino)pyridine). a) Fragment of the coordination polymer showing the main zig-zag pattern and the dmap and acetate molecules. b) View of the Hg environment; the organic ligands and the ClO_4^- anions have been omitted for clarity. Selected bond lengths [Å]: Hg(1)–N(1), 2.051(6); Hg(1)–O(1), 2.640(4); Hg(2)–N(3), 2.070(6); Hg(2)–N(5), 2.074(6); Hg(2)–O(1), 2.508(4); Hg(2)–Hg(2), 3.4965(7). Selected bond angles [°]: N(1)–Hg(1)–N(1)^{i}, 180.000(1); N(1)–Hg(1)–O(1), 87.57(19); N(1)–Hg(1)–O(1)^{i}, 92.43(19); O(1)–Hg(1)–O(1), 180.000(1); N(3)–Hg(2)–N(5), 170.8(2); N(3)–Hg(2)–O(1), 95.21(19); N(5)–Hg(2)–O(1), 93.15(19); N(3)–Hg(2)–Hg(2), 97.26(15); N(5)–Hg(2)–Hg(2), 84.40(16); O(1)–Hg(2)–Hg(2), 103.34(10). Superscripts (i) indicate the symmetry $(-x, -y, -z)$.

to-face' types [11–13]. As shown in the projection of *Fig. 5*, an overall 'slipped' stacking is observed, which can be rationalized qualitatively in terms of optimizing approaches between atoms of opposite charges [14]. In the crystal reported here, the interplanar distance is *ca.* 3.49 Å between two Hg(2) atoms, which is appreciably shorter than in normal π/π stacking [15][16]. The interplanar distance between Hg(1) and Hg(2) is *ca.* 3.64 Å.

In summary, the self-assembly in the coordination complex **1** is governed by Hg–Hg interactions, weak O–Hg interactions, and aromatic π/π interactions, giving rise to a one-dimensional polymer. Whether the Hg–Hg interactions help to form the O–Hg contacts, or *vice versa*, is not clear, however.

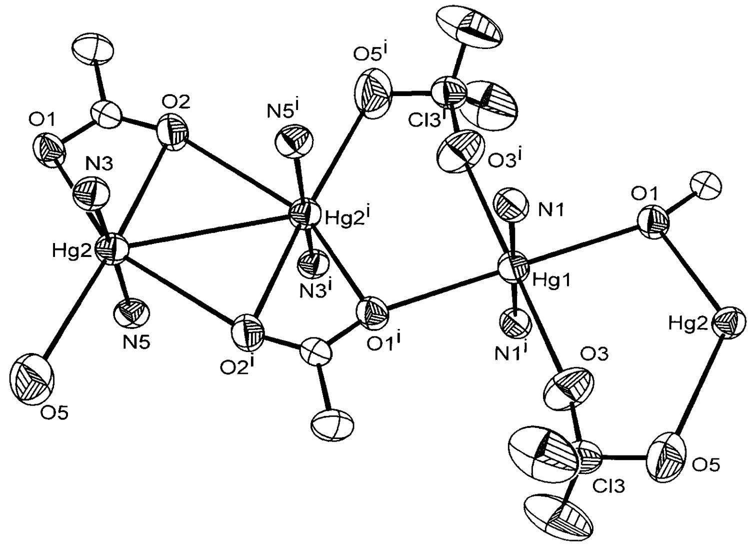

Fig. 3. *Bonding interactions made visible for a fragment of the polymeric complex* **1** *after extending the bonding limit to* <3.1 *Å* (see text)

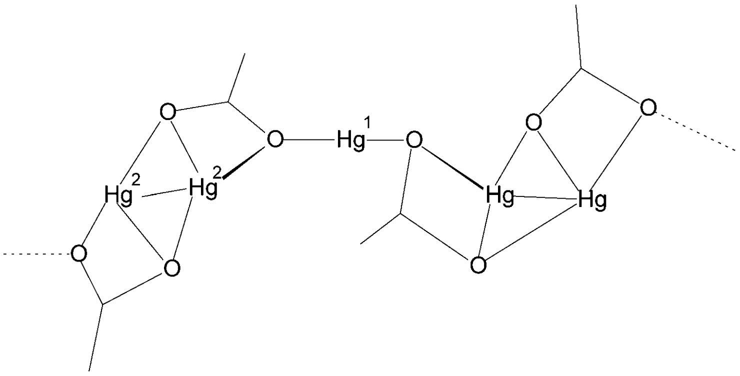

Fig. 4. *Array of Hg-atoms in complex* **1** *both bonded to and bridged by acetate units* (see text)

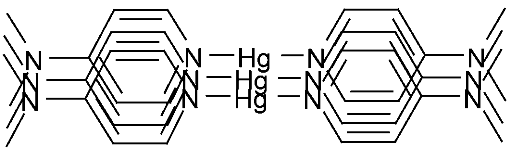

Fig. 5. *Projection of nearest-neighbor pairs in the* π/π *stacks of heteroaromatic bases of complex* **1**

Experimental Part

The complex $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n\{(ClO_4)_4\}_n$ (**1**) was prepared by the branch-tube method. dmap (0.122 g, 1 mmol) was placed in one arm of a branched tube, and a 1:2 mixture of $Hg(OAc)_2$ (0.160 g, 0.5 mmol) and $NaClO_4$ (0.123 g, 1 mmol) in the other. Then, MeOH was carefully added to fill both arms, the tube was sealed, and the ligand-containing arm was immersed in a bath at 60°, while the other arm was kept at r.t. After 2 d, white crystals had deposited in the colder arm. They were filtered off, washed with acetone and Et_2O, and dried in air to afford 0.107 g (35%) of **1**. M.p. 205°. IR (selected bands; in cm^{-1}): 618*m*, 806*s*, 1000v*s*, 1108v*s*, 1224*m*, 1399*m*, 1534*s*, 1610*s*, 2905*w*, 3040*w*. ^{1}H-NMR ((D_6)-DMSO; δ in ppm): 1.95 (*s*, 1 H); 3.10 (*s*, 6 H); 6.95 (*d*, 2 H); 8.20 (*d*, 2 H). ^{13}C-NMR ((D_6)-DMSO): 22.75; 107.82; 149.23; 155.68; 178.80. Anal. calc. for $C_{46}H_{66}Cl_4Hg_3N_{12}O_{20}$: C 29.60, H 3.50, N 9.20; found: C 29.82, H 3.56, N 9.07.

X-Ray Crystal-Structure Analysis. Crystallographic measurements were conducted at 293(2) K on a *STOE IPDS II* diffractometer. Intensity data were collected within the range $1.88° \leq \theta \leq 25.88°$ with graphite monochromated MoK_α radiation for a crystal of dimension 0.33 × 0.26 × 0.22 mm. The structure was solved by direct methods (SIR97) [17], and refined by full-matrix least-squares techniques on F^2 (SHELX97) [18]. Plots were generated with ORTEP III [19], and WinGX [20] was used as an interface during the structure-solution procedure. Numerical absorption correction was applied.

Crystal data: formula, $C_{23}H_{33}Cl_2Hg_{1.50}N_6O_{10}$; M_r 925.34 g/mol; triclinic system, space group $P\,\bar{1}$; $a = 9.2730(10)$, $b = 10.9400(13)$, $c = 16.6940(16)$ Å; $\alpha = 86.560(10)$, $\beta = 79.097(10)$, $\gamma = 82.550(10)°$; $V = 1647.38(3)$ Å^3; $D_c = 1.865$ Mg/m^3 ($Z = 1$); $F(000) = 894$; $R(wR) = 0.0379$ (0.0826) for 4745 reflections, with $I > 2\sigma(I)$; $R(wR) = 0.0578$ (0.0886) for all data.

The crystallographic data (excluding structure factors) for **1** have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as supplementary publication number CCDC-251137. Copies of the data can be obtained, free of charge, by application to *CCDC*, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

Support of this work by the Tarbiat Modarres University is gratefully acknowledged.

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Received December 7, 2004