Tetrazine-Based Ligand Transformation Driving Metal–Metal Bond and Mixed-Valence Hg$^1$/Hg$^{	ext{II}}$

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Supporting Information

ABSTRACT: Understanding the self-assembly of cluster aggregates remains an important challenge in coordination chemistry. A chelating tetrazine-based ligand was employed to isolate an unprecedented tetranuclear Hg$_4$ complex exhibiting Hg$^1$/Hg$^{	ext{II}}$ mixed valence, which also contains metal–metal bonds. Single-crystal X-ray diffraction, X-ray photoelectron spectroscopy, solid-state nuclear magnetic resonance, and theoretical approaches (density functional theory) were employed to shed some light on the structure and self-assembly of this discrete molecule.

INTRODUCTION

Coordination cluster aggregates formed via self-assembly continue to attract attention from the scientific community for their aesthetic beauty, complexity, and intrinsic physical properties. A large number of such molecules have been reported over the past few decades with various nuclearities and sizes, some of which even rival small nanoparticles in size. In the synthesis of molecular cluster aggregates, serendipity plays a significant role. However, directed self-assembly can be used for small nuclearity complexes, thanks to carefully designed ligand scaffolds and careful control of reaction conditions. First and foremost, organic ligands can act as chelates and bind to metal ions, but they can also become templates, bridging units, and/or electron reservoirs. Ligands can also play a symbiotic relationship with metal ions by sharing electrons and stabilizing the unstable oxidation states of metal ions. Since the discovery of coordination complexes, chemists have continued to create new systems with tailored properties through carefully designed ligand frameworks. With that said, serendipitous formation of unexpected complexes continues to fascinate researchers, as discovering their formation provides unique opportunities to understand the self-assembly process and target the desired molecules.

To that end, tetrazines have shown tremendous potential in coordination chemistry as they can effectively bind to multiple metal ions while also acting as bridging units and electron reservoirs. Furthermore, the redox properties of tetrazines have proven ideal for providing strong exchange-coupling pathways in magnetic materials. Indeed, under certain synthetic conditions, a metal-assisted ring opening of the tetrazine ring can be observed, leading to unpredicted structures.

As an element, mercury displays unique structural features upon coordination. The Hg–Hg bond has been studied for decades and was the first metal–metal bond uncovered for group 12 elements. Mercury has a large ionization energy due to relativistic stabilization of the 6s orbital, resulting in strong Hg–Hg bonds. However, because of instability, most metal–metal bonded complexes were isolated under an inert atmosphere using the organometallic approach. Although mixed oxidation states of Hg-based compounds exist, they are relatively rare in coordination compounds. With this in mind, we have focused our attention on the coordination chemistry of Hg complexes using the tetrazine-based 3,6-di(pyrimidin-2-yl)-1,2,4,5-tetrazine (BpymTz) ligand. As such, we aim to promote the self-assembly of coordination cluster aggregates through the use of multidentate tetrazine and investigate their structural formation. Herein, we present a tetranuclear (Hg$_4$) coordination complex with unique structural features, such as Hg–Hg bond formation as well as mixed Hg$^1$/Hg$^{	ext{II}}$ oxidations states.

RESULTS AND DISCUSSION

The reaction of Hg(CH$_3$COO)$_2$·6H$_2$O (4 equiv) with 3,6-di(pyrimidin-2-yl)-1,2,4,5-tetrazine (BpymTz) (2 equiv) in...
N,N-dimethylformamide (DMF) gives a clear orange solution after stirring for several minutes. After 3 days, yellow needlelike crystals of [Hg\(_2\)Hg\(_{3}\)(L\(_{-}\))(CH\(_3\)COO)\(_4\)](DMF)\(_2\) (I) were isolated in 70% yield. Single-crystal X-ray diffraction (SCXRD) studies reveal the ring opening of the central tetrazine moiety of the ligand, which under these conditions leads to the hydrolyzed anionic ligand L\(^{-}\) (see Figure 1 and

Figure 1. Molecular structure of I (top) highlighting the coordination environment of Hg metal ions. Packing arrangement of I (bottom) showing close intermolecular metal–metal contact (blue dashed lines) in the supramolecular Hg\(_8\) unit. Color code: Hg (green), N (blue), O (red), and C (gray). Hydrogen and solvent molecule were omitted for clarity.

Supporting Information Tables S1–S3). It is noteworthy that any attempts to isolate any other complexes using different metal salts to probe the anion effect on structure formation was unsuccessful. Moreover, the use of various solvents also did not afford any solid material, thus highlighting the importance of the coordinated DMF molecule in structural formation.

The structure of I, which crystallizes in the triclinic space group P\(_{\text{I}}\), consists of a distorted planar molecule with two L\(^{-}\) ligands and four mercury metal ions. Here, Hg\(_1\) and Hg\(_4\) are situated at the edge of the compound while Hg\(_2\) and Hg\(_3\) reside in the center (Figure 1). These ligands L\(^{-}\) lie within the plane of compound I and are inverted with respect to each other, thereby framing Hg\(_2\) and Hg\(_3\). The coordination environment of Hg\(_1\) and Hg\(_4\) are heptacoordinate with highly distorted geometries, where four coordination sites are occupied by O-donors from two CH\(_3\)COO\(^{-}\) anions, with the remaining positions filled by three donor atoms from the L\(^{-}\) ligand, two N atoms, and one O atom. The five-coordinate Hg\(_2\) and Hg\(_3\) atoms adopt a highly distorted square-based pyramidal geometry with two L\(^{-}\) ligands coordinating equatorially (N- and C-donor atom) and the axial portion occupied by a DMF solvent molecule. A close look at the packing arrangements reveals that each {Hg\(_4\)} unit faces a neighboring molecule leading to weak metal–metal interactions (4.08 Å, Figure 1 bottom), thereby forming a supramolecular octanuclear complex. All four heptacoordinated and pentacoordinated metal ions are symmetrically distinguishable, and thus their geometries are distorted differently because of varying bond lengths and angles (see Tables S2 and S3).

The BpymTz ligand transformation in situ results in two new anionic L\(^{-}\) ligands that act as a template for four Hg ions and drives a direct metal–metal bond between the central metal ions. As shown in Figure 1, the \(=\text{N}–\text{N}=(\text{N}2\text{N}4\text{N}9\text{N}10\text{N})\) fragment connecting two bipyrimidine substituents is a result of the tetrazine ring cleavage. Furthermore, the presence of the C=O group in one of the terminal positions of the fragment indicates metal-assisted hydrolysis, thereby producing a ring opening. Observations such as these have already been reported in tetrazine-based ligands,\(^{4a,4b}\) however, instead of two C=O or C–OH groups in the extremities of the fragment, only one carboxyl is formed along with an unprecedented carbanion in the opposite side.

In I, SCXRD analysis reveals a Hg–Hg bond distance of 2.99 Å between Hg\(_2\) and Hg\(_3\). Although this distance exceeds the typical Hg–Hg bond length of 2.50–2.52 Å, longer metal–metal bond distances are common with organometallic compounds where distances of 2.61, 2.66 Å, and even 2.71 Å have been reported for Hg–Hg bonds.\(^{4c}\) Furthermore, literature pertaining to mercury triangles and rings clusters describe Hg–Hg bond lengths from 2.77 to 3.16 Å.\(^{8}\)

The elongation in the metal–metal bond in I is likely due to steric-related stress imposed by the coordinated DMF solvent molecules. Because Hg\(^{II}\) ions forming metal bonds are rare, Hg\(_2\) and Hg\(_3\) can be assigned, as Hg\(^{II}\) forms the well-known dication \([\text{Hg}^{II}_2]\)^{2+}.\(^{9}\) This is consistent with the charge-balance considerations as well as the presence of a lower coordination geometry, which is typically assigned to Hg\(^{I}\) oxidation states in Hg\(^{II}/Hg^{IV}\) mixed-valence clusters.\(^{9}\) When considering the charge balance of Hg\(_1\) and Hg\(_4\), bond valence sum (BVS) calculations indicate that the outermost metal ions of the compound are Hg\(^{II}\) (Hg\(_1\) = 1.80 and Hg\(_4\) = 2.13). BVS calculations could not be performed on Hg\(_2\) and Hg\(_3\) because no reference values have been reported for an Hg–C bond.\(^{10}\) Moreover, each azo bis-pyridine ligand contributes a charge of \(-1\) because of the presence of the carbanion, with the overall charge of the complex being balanced by the four CH\(_3\)COO\(^{-}\) counterions.

To shed some light on the physical properties of I, spectroscopic analysis was performed. Ultraviolet–visible (UV–vis) spectroscopy was carried out to elucidate the electronic structure of the compound. Analysis of Figure S1 reveals two peaks around 200 and 250 nm, which are associated with ligand–π-electron transitions. A broad absorption peak can be observed around 350 nm, which is attributed to coordinated Hg ions.\(^{10}\) X-ray photoelectron spectroscopy (XPS) was used to validate the oxidation state of the metal ions and the structural composition. The results indicate a peak at binding energies of 101.5 and 105.7 eV, which are associated with Hg 4f\(_{7/2}\) and 4f\(_{5/2}\) levels, respectively (Figure S2). Despite this close energy gap, the results confirm the presence of Hg\(^{II}\) and Hg\(^{III}\) ions.\(^{11}\) Satellite peaks are also observed at 108.8 and 112.6 eV and can be associated with the differential charging effects, as previously reported in the literature.\(^{12}\) \(^{199}\)Hg solid-state nuclear magnetic resonance (NMR) experiments were performed to support the single-
crystal X-ray data, which reveals broad peaks around 1519.6 ppm that indicate the presence of Hg (Figure S3). Nonetheless, attempts to assign $^{199}$Hg–$^{199}$Hg coupling were unsuccessful. Superconducting quantum interference device magnetic measurements were also performed to verify the magnetic nature of 1. No paramagnetic signal was observed at 300 K under an applied field of 0.1 T. This is presumably because of the unpaired electron in the outermost 6s orbital of the Hg atom pairing up with that of the other Hg atom through the formation of the covalent Hg–Hg bond.

To gain more insight into the thermodynamics of the reaction and on the electronic structure of the final compound 1, computations at the density functional theory (DFT) level, accounting implicitly for solvation, were performed. According to our hypothesis (Figure 2), the initial tetrazine ligand (BPymTz) is first hydrolyzed and coordinated to Hg$^{II}$, as these ions may play an important role in the catalysis of the hydrolysis reaction. The irreversible hydrolysis reaction is highly exothermic (−56 kcal/mol) because of the formation of N$_2$, whereas coordination is only exothermic by 2 x −3 kcal/mol, suggesting an equilibrium process (Figure 2, 1a). The next step groups together several elementary reactions, ranging from deprotonation (by acetate) to dimerization, which results in 1b. Given the complexity of the self-assembly reaction mechanism and to avoid extensive reaction network analysis, the reaction mechanism was kept minimal. Ultimately, deprotonation and dimerization are exothermic by −20 kcal/mol. The final complex 1c includes two coordinated DMF molecules in the crystal structure. Computational results suggest that they are rather weakly bound (−12 kcal/mol), given that the loss of translational and rotational entropy was not accounted. However, experimentally, the complex crystallizes spontaneously, which on the one hand stabilizes it further and on the other hand explains the inclusion of solvent molecules to fill the otherwise void space.

The Hg–Hg bond is, with the experimental length of 2.99 Å (2.88 Å computed), rather long compared to 2.49 Å in HgBr$_2$ and 3.0 Å in metallic Hg. Therefore, the nature of the Hg dimer is clarified by analyzing the atomic charges of the N donor in trans position to the C donor: if they are neutral, donating N atoms, the core is indeed a {Hg$^{	ext{I}}$}$_2$Å entity. Because atomic charges are noumenons, but still carry valuable information, the charges of both the Hg and the N atoms are determined with two very distinct but robust schemes: quantum theory of atoms in molecules (QTAIM), which only depends on the electron density and CMS, which is fitted to reproduce gas-phase dipole moments. With QTAIM, all eight nitrogen atoms that are coordinated to an Hg atom have a negative charge of about 0.8 e$^-$, suggesting that they are all roughly equivalent as ligands. For the Hg atoms, QTAIM identifies partial charges of 0.8 and 1.2 e$^-$, suggesting {Hg$^{	ext{I}}$}$_2$Å and Hg$^{	ext{II}}$, respectively. CMS shows a similar trend: the central N atoms coordinating the Hg dimer are charged-0.1 e$^-$, whereas the N atoms of the pyrimidine are charged by-0.2 e$^-$. Furthermore, the charges on Hg are 0 and 0.3 e$^-$, with the difference between them being in close agreement with the QTAIM results. Hence, the atomic charges are in agreement with neutral nitrogen donors, a central {Hg$^{	ext{I}}$}$_2$Å entity, and peripheral Hg$^{	ext{II}}$. The electrons to reduce Hg$^{	ext{II}}$ are, formally, provided by the transformation of deprotonated N-atoms to neutral N donors.

### CONCLUSIONS

In summary, a combination of tetrazine-based ligand and mercury acetate yielded an unprecedented mixed valence Hg$^{	ext{I}}$/Hg$^{	ext{II}}$ tetranuclear complex with a central metal–metal bond promoted by ligand transformation. Solution and solid-state analysis confirm the molecular structure. DFT calculations support the applied characterization methods, and the computational results suggest the energetically favorable mechanism of the compound formation beginning with the hydrolysis of BpymTz, which results in tetrazine ring opening followed by {Hg$^{	ext{I}}$}$_2$Å dimerization. The results presented in this work represent a new perspective on the coordination chemistry and self-assembly of late transition metals.

### ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01861.

Materials and synthesis description, physical measurements, and XPS, UV–vis, and solid-state NMR spectroscopy plots (PDF)
Crystallographic data for 1 (CIF)

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**Notes**
The authors declare no competing financial interest.

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