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Silver(I) and Mercury(II) Complexes with 1-Methyl-1,2,4-triazole as Models for Metal-Mediated Base Pairs – Formation of Discrete Complexes in Solution vs. One- and Two-Dimensional Coordination Polymers in the Solid State

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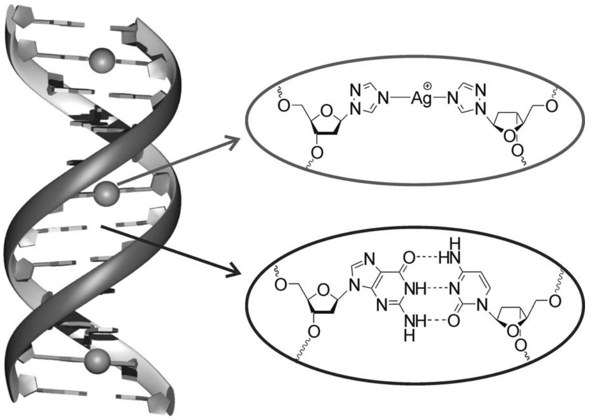
Dedicated to Stephen J. Lippard on the occasion of his 70th birthday

Keywords: Silver / Mercury / N ligands / Metal-mediated base pairs / Coordination polymers

The coordination chemistry of 1-methyl-1*H*-1,2,4-triazole (1-mtri) with respect to the linearly coordinating metal ions silver(I) and mercury(II) has been established. The ligand serves as a model nucleobase for the artificial 1,2,4-triazole nucleoside. Solution studies show that 2:1 complexes are formed with both metal ions in water. Mercury(II) forms more stable complexes than silver(I), with a stability constant of $\log\beta_2$ of 10.5 ± 2.5 vs. 4.3 ± 0.4 for the silver(I) complex. In the solid state, different types of cationic coordination polymers are formed. The silver complex [Ag(1-mtri)](ClO_4) (**1**) comprises a one-dimensional coordination polymer $[Ag_2(1\text{-mtri})_2]_n^{2n+}$, showing a 1:1 ratio of ligand to metal. By contrast, the mercury complex [Hg(1-mtri)$_2$](ClO_4)$_2$ (**2**) retains a 2:1 stoichiometry while forming a two-dimensional coordination polymer. In compound **2**, mercury(II) is coordinated in a distorted octahedral fashion, with two normal and four long bonds, resulting in a compressed octahedron.

Introduction

The introduction of metal-mediated base pairs into nucleic acids is a convenient method for the functionalization of this versatile self-assembling biomolecule.[1] In this type of artificial base pair, the hydrogen bonds present in their natural counterparts are replaced by coordinative bonds to a central metal ion (Scheme 1). Over the last few years, several artificial nucleosides have been developed.[2–7] In particular, azole-based nucleosides have proven to be excellent building blocks for metal-modified DNA.[8] Recently, we determined the structure of a short oligonucleotide duplex comprising three central, contiguous imidazole–Ag^I–imidazole base pairs, thereby proving that the B-type nucleic acid conformation is compatible with the presence of metal-mediated base pairs.[8c] Moreover, an interesting conformational change from hairpin to regular double helix, induced by the formation of metal-mediated base pairs, was first established using a 1,2,4-triazole nucleoside.[8b] Additional investigations showed that this conformational change can also be observed in RNA.[9]



Scheme 1. Representation of a B-type DNA duplex with natural hydrogen-bond-mediated and artificial metal-mediated base pairs (reproduced with permission from ref.[1a]).

In the context of metal complexes of the artificial 1,2,4-triazole nucleoside, previous reports suggested a 2:1 stoichiometry for the silver(I) complex (as necessary for the formation of a base pair), whereas a 1:1 ratio between ligand and metal ion was reported for mercury(II).[8a] We therefore set out to determine the molecular structures of the respective metal complexes, substituting the artificial nucleoside by its "model nucleobase" 1-mtri. In addition, the solution studies were repeated to ensure that the reactivity of 1-mtri resembles that of the corresponding nucleoside.

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Results and Discussion

Solution Studies of 1-Methyl-1*H*-1,2,4-triazole

To determine the stoichiometry of complexes formed from 1-mtri with silver(I) and mercury(II), ^{1}H NMR experiments were carried out in which solutions of 1-mtri in D_2O were titrated with $AgClO_4$ and $Hg(ClO_4)_2$, respectively. These metal ions were chosen because they are well known for their typically linear coordination geometry. The changes in chemical shift of the aromatic protons were monitored, and, by applying the method of continuous variations,[10] Job plots were obtained (Figure 1, a). Interestingly, the formation of stable 2:1 complexes is suggested for both metal ions, indicated by the asymmetric shape of the plots with a maximum value at a molar fraction $\chi_{1\text{-mtri}}$ of about 67%. This appears to contradict previous investigations in which a 1:1 stoichiometry was observed for the complex between mercury(II) and the 1,2,4-triazole nucleoside.[8a] Two explanations are possible for this apparent inconsistency: a) the nucleoside and model nucleobase show different metal binding properties; b) the influence of the counterion needs to be considered. Identical anions have been used in the present study (namely perchlorate), whereas previous studies have used $AgNO_3$ and $Hg(CF_3COO)_2$. Moreover, previous experiments with mercury(II) were performed in triethylammonium acetate buffer whereas unbuffered solvent was used for silver(I). No buffers were used in this study. Instead, the pD values were checked prior to and after the titration to ensure that the observed chemical shift changes were not the result of a protonation of the ligand. Hence, the counterion explanation seems to be more plausible, showing that 1,2,4-triazole should also be capable of forming metal-mediated base pairs with mercury(II). In fact, control experiments suggest that the 1:1 stoichiometry previously observed for the Hg^{II}–1,2,4-triazole nucleoside system was indeed a result of the presence of the acetate-containing buffer. The 1-mtri ligand used in the present study also forms 2:1 complexes with $Hg(NO_3)_2$ and $Hg(CF_3COO)_2$ (Supporting Information). In the presence of (excess) triethylammonium acetate buffer (pH 7), however, a 1:1 complex is formed (see Supporting Information), suggesting that the acetate anions directly compete with the 1-mtri ligand. A related observation showing that the type of anion present in solution influences the composition of the products has recently been reported for pyridine complexes of mercury(II) halides.[11]

Having deduced the formation of 2:1 complexes in solution, additional titrations of the ligand with increasing amounts of metal ion were performed and monitored by ^{1}H NMR spectroscopy (Figure 1, b). Based on these data and those from the Job plots, stability constants for the metal complexes were determined by using nonlinear least-squares regression implemented in the program EQNMR.[10,12] The results are given in Table 1.

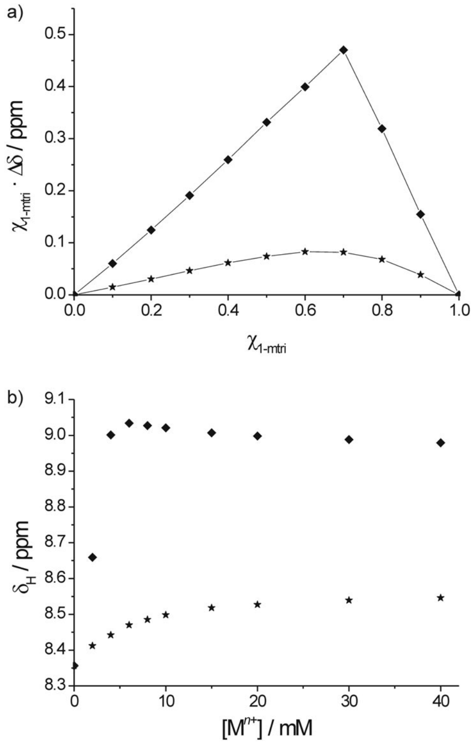

Figure 1. a) Representative Job plots for the treatment of 1-mtri with $AgClO_4$ (★) and $Hg(ClO_4)_2$ (◆); b) titration of 1-mtri with $AgClO_4$ (★) and $Hg(ClO_4)_2$ (◆). The chemical shift reported in this figure is that of H5. The complete data can be found in the Supporting Information.

Table 1. Stability constants for metal ion complexes of 1-mtri.[a]

	Silver(I) complex		Mercury(II) complex	
	logβ_1	logβ_2	logβ_1	logβ_2
1-mtri	2.0 ± 0.2	4.3 ± 0.4	5.6 ± 1.3	10.5 ± 2.5
Nucleoside[8a]	1.5 ± 0.7	4.3 ± 0.1	1.56 ± 0.04	–

[a] The error values correspond to three times the standard deviations of the mean values. The measurements were performed at T = 300 K.

As expected, the stability constants of the silver(I) complexes of the model nucleobase 1-mtri and the corresponding artificial nucleoside are identical within error limits. This clearly indicates that results obtained from experiments with the model nucleobase can be transferred to the nucleoside. The stability constants of the mercury(II) complexes of these two ligands cannot be compared because of the influence of coordinating vs. noncoordinating anions. Moreover, as can be deduced from the relatively large error values in the case of mercury(II), the NMR titration method reaches its limits for highly stable metal complexes. This observation is in good agreement with previous investigations that suggested that individual stability constants of $\log K_i > 5$ cannot be determined by this method.[10c]

Solid-State Structure of the Silver(I) Complex

In order to elucidate the molecular structures of the metal complexes of 1-mtri and thereby get a first experimental insight into the possible structure of a metal-mediated base pair involving 1,2,4-triazole nucleoside, 1-mtri was treated with $AgClO_4$ and $Hg(ClO_4)_2$, respectively, on a preparative scale. Interestingly, the silver(I) complex isolated this way does not adopt the 2:1 stoichiometry observed in the solution studies, irrespective of whether the starting materials were allowed to react at a 1:1 or 2:1 ratio. Instead, a one-dimensional cationic coordination polymer $[Ag_2(1\text{-mtri})_2]_n^{2n+}$ is formed (Figure 2). The fact that the solution and solid-state structures differ from each other is not unusual and has been observed for other silver(I) complexes with triazole-derived ligands.[13] In the solid-state structure of $[Ag(1\text{-mtri})](ClO_4)$ (**1**), the 1,2,4-triazole moieties are bridged by silver(I) ions with linear N4–Ag2–N4b and slightly bent N2–Ag1–N2a bridges. The Ag–N distances are in the normal range (Table 2). A closely related coordination polymer structure has been observed for the cation $[Ag_2(3\text{-amino-1,2,4-triazole})_2]_n^{2n+}$, albeit comprising linear N–Ag–N bridges only.[14] The linearly coordinated fragment of the coordination polymer **1** with its coplanar ligands resembles the geometry expected for a metal-mediated base pair (except for the *trans*-oriented methyl groups which should be *cis*-oriented in the context of B-type DNA). The fact that a calculated gas-phase structure of the base pair comprises the ligands oriented almost perpendicular to each other suggests a rather low energy barrier for the rotation around the Ag2–N4 axis.[15]

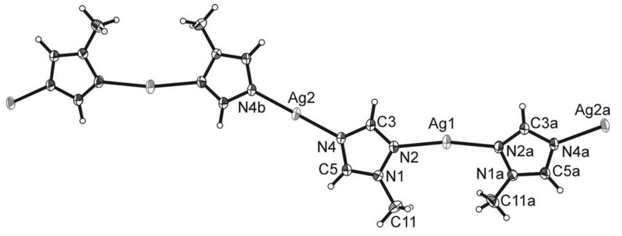

Figure 2. Section of the one-dimensional coordination polymer $[Ag(1\text{-mtri})](ClO_4)$ (**1**) including atom numbering scheme The anions have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

Table 2. Selected interatomic distances [Å] and angles [°] for compound **1**.

Ag1–N2	2.181(2)	Ag2–N4	2.164(2)
Ag1–O11	2.577(9)	Ag2–O21	2.77(3)
Ag1a–O11	2.649(9)		
N2–Ag1–N2a	169.0(1)	N4–Ag2–N4b	180.00(6)
Ag1–O11–Ag1a	101.8(3)	O21–Ag2–O21a	180.0

Figure 3 shows the layer structure formed by neighbouring coordination polymers. On first inspection, the silver(I) ions appear to be arranged in a linear fashion (Figure 3, a). However, a view down the crystallographic *c* axis clearly demonstrates that the Ag1 atoms of neighbouring layers are oriented in a zigzag fashion, whereas the Ag2 atoms are indeed arranged linearly (Figure 3, b). The Ag···Ag distance along these linear metal arrays is 3.5971(3) Å. Considering the van der Waals radius of a silver atom to be 1.72 Å,[16] this distance is slightly too large to account for an argentophilic interaction. The reason for the different arrangement of the silver(I) ions is most likely related to the presence of the perchlorate counterions. As seen in Figure 4, the Ag1 ions of neighbouring layers are bridged by pairs of perchlorate ions in a slightly asymmetrical μ-κ*O* fashion. In contrast, the linearly arranged Ag2 ions are bridged by single perchlorate ions in a μ-κ^2*O*,*O′* fashion. The Ag–O bond lengths are 2.557(9) and 2.649(9) Å for Ag1 and 2.77(3) for Ag2 (Table 2). The latter distance suggests a comparatively weak bond, whereas the values for Ag1 are in the range typically found for perchlorate ions engaged in this binding mode.

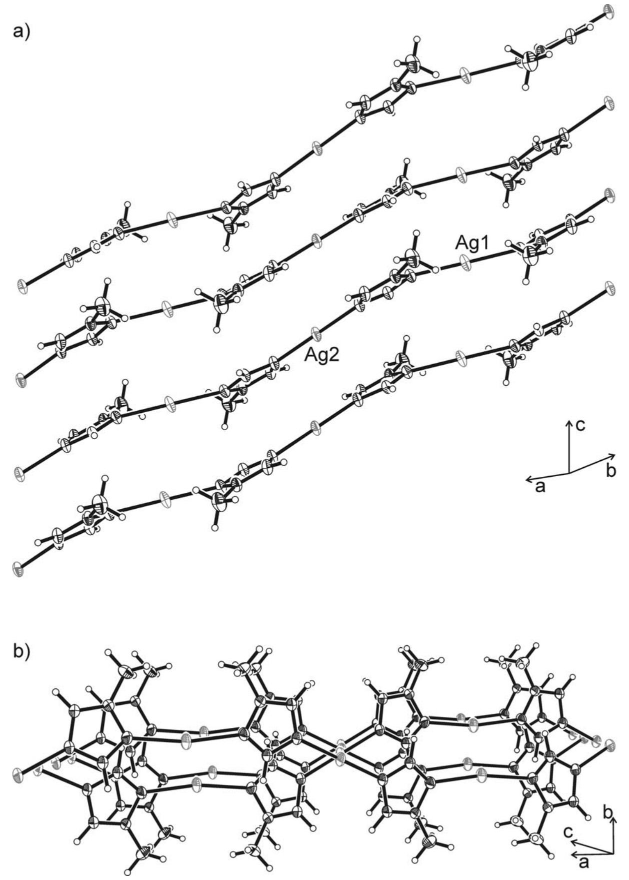

Figure 3. a) Packing of **1** showing a layered arrangement of the one-dimensional coordination polymer; b) view along the crystallographic *c* axis. Displacement ellipsoids are drawn at 50% probability level.

Solid-State Structure of the Mercury(II) Complex

When reacting 1-mtri with $Hg(ClO_4)_2$ on a preparative scale, a crystalline product of the composition $[Hg(1\text{-mtri})_2](ClO_4)_2$ (**2**) was obtained. Hence, the resulting compound has the same 2:1 stoichiometry as observed in solution. Part a of Figure 5 shows the molecular structure of the $[Hg(1\text{-mtri})_2]^{2+}$ building block of **2**. The mercury(II) ion is coordinated linearly by two 1-mtri ligands via their N4 nitrogen atom. The Hg1–N4 bond length of 2.046(2) Å is in the normal range (Table 3). Interestingly, the metal ion forms four additional, rather long bonds. In particular, two 1-mtri ligands from neighbouring $[Hg(1\text{-mtri})_2]^{2+}$ units bind via

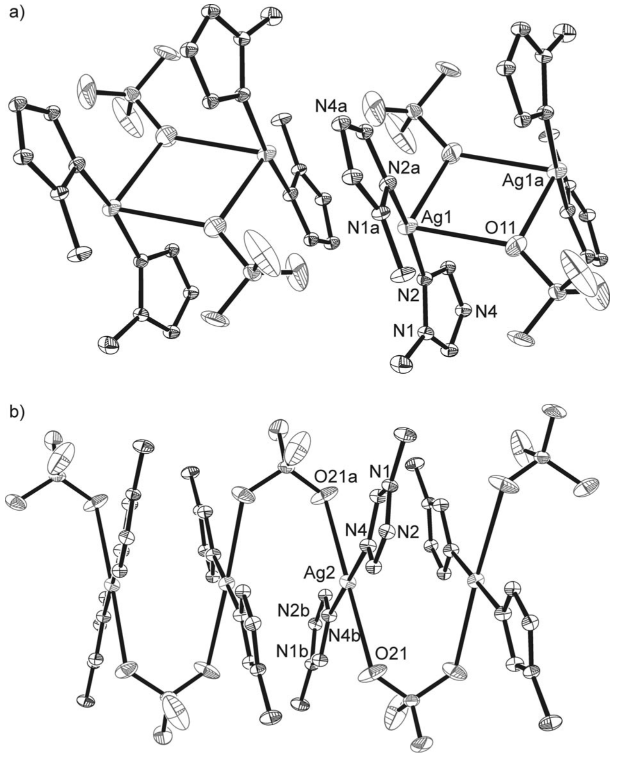

Figure 4. Sections of the structure of the cationic coordination polymer **1** including selected counterions. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms have been omitted for clarity; a) coordination environment of Ag1; b) coordination environment of Ag2.

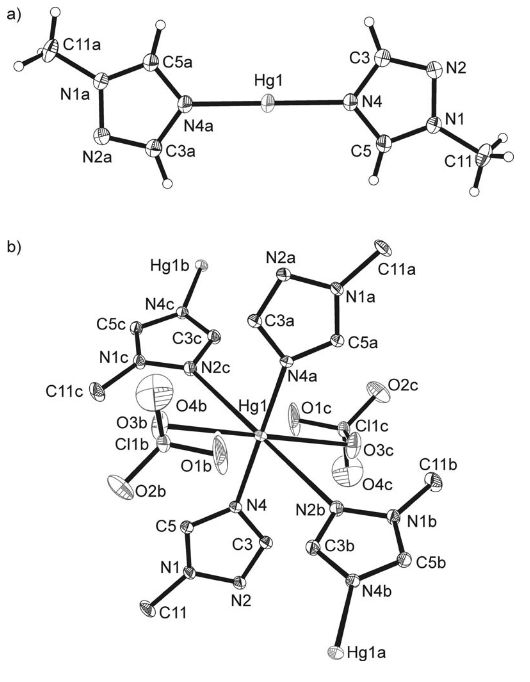

Figure 5. a) Molecular structure of the $[Hg(1\text{-mtri})_2]^{2+}$ building block of the two-dimensional coordination polymer **2**. Displacement ellipsoids are drawn at 50% probability level; b) coordination environment of the mercury(II) ion in **2**, including weakly bonded ligands at longer distances. Only one position of the disordered perchlorate is shown. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected interatomic distances [Å] and angles [°] for compound **2**.

Hg1–N4	2.046(2)	Hg1–N2b	2.888(2)
		Hg1–O3b	2.802(9)
N4–Hg1–N4a	180.0	N4–Hg1–N2b	81.10(8)
N2b–Hg1–N2c	180.0	N4–Hg1–O3b	89.9(2)
O3b–Hg1–O3c	180.0	N2b–Hg1–O3b	109.5(2)

their N2 atoms with an unusually long Hg1–N2b distance of 2.888(2) Å. Moreover, two perchlorate ions bind in a monodentate fashion with long Hg1–O3b distances of 2.802(9) Å (Figure 5, b). Considering the van der Waals radius of mercury to be at least 1.55 Å,[16] the Hg–O and Hg–N contacts can be considered as bonding interactions. The coordination sphere can best be described as a "compressed" octahedron with two normal and four unusually long bonds. In this structure, the mercury(II) ion is coordinated by six distinct, nonchelating ligands. Interestingly, a related compound comprising 3-methyl- and 3,5-dimethyl-1,2,4-triazole plus mercury(II) has one of its metal ions in a very similar environment, albeit with significantly shorter bonds.[17] In this compound, all three nitrogen atoms of both ligands are accessible for mercury(II) binding, so that a three-dimensional coordination polymer is formed. Contrary to this, and probably as a result of the fact that only two nitrogen atoms are available for metal ion binding, the structure of **2** in the solid state can best be described as a two-dimensional coordination polymer (Figure 6).

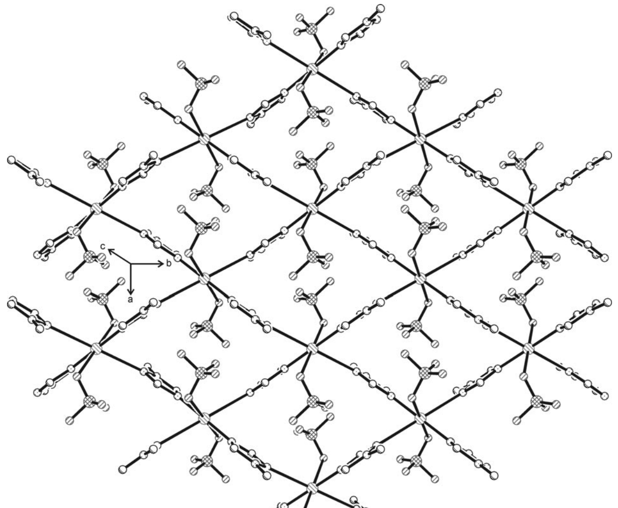

Figure 6. Two-dimensional coordination network formed from **2**. Only one position of the disordered perchlorate is shown. Hydrogen atoms have been omitted for clarity.

Conclusions

An investigation of the metal ion complexation behaviour of the ligand 1-mtri, serving as a model nucleobase for the artificial 1,2,4-triazole nucleoside, shows that 2:1 complexes are formed with $AgClO_4$ and $Hg(ClO_4)_2$, respec-

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tively. The stoichiometry of these complexes resembles that of metal-mediated base pairs.[1] An apparent contradiction to previously published results[8a] is most likely explained by the absence of acetate ions (from a buffer system) that would otherwise compete with 1-mtri for mercury(II) coordination sites. Determination of the stability constants revealed that the mercury(II) complex is significantly more stable than the corresponding silver(I) complex. This differential stability also becomes manifest in the solid-state structures of the complexes: The less stable silver(I) complex dissociates to form an interesting one-dimensional coordination polymer cation $[Ag_2(1\text{-mtri})_2]_n^{2n+}$ with a 1:1 stoichiometry of ligand and metal ion. In contrast, the mercury(II) complex retains its 2:1 stoichiometry in the solid state. The two-dimensional coordination polymer that is formed in this case comprises an octahedrally coordinated metal ion with two normal and four long bonds. A closer look at the structural details of both coordination polymers shows that the $[Ag(1\text{-mtri})_2]^+$ and $[Hg(1\text{-mtri})_2]^{2+}$ moieties are arranged in the fully planar fashion that is required for the incorporation as a metal-mediated base pair into a nucleic acid. Moreover, the combination of solution studies and X-ray single crystal diffraction analyses demonstrates that the stability constants of complexes present in solution can have a significant impact on the type of network structure formed upon crystallization. It is important in the context of structure prediction to consider stability constants when attempting to change only the metal centre within a given network structure.

Experimental Section

General: The ligand 1-mtri was synthesized according to a published procedure.[18]

***Caution*:** Perchlorate salts of metal complexes with organic ligands are potentially explosive!

Synthesis of $[Ag(1\text{-mtri})](ClO_4)$ (1): To a solution of 1-mtri (26.8 mg, 323 µmol) in H_2O (2 mL) was added a 0.405 M solution of $AgClO_4$ in H_2O (0.798 mL). The resulting suspension was stirred at ambient temperature in the dark for 24 h. The resulting precipitate was collected by filtration, washed with cold H_2O (1 mL) and dried at 40 °C. After recrystallization from H_2O, **1** was obtained as colourless needles (47.5 mg, 164 µmol, 51 %). $C_3H_5AgClN_3O_4$ (290.41): calcd. C 12.4, H 1.7, N 14.5; found C 12.5, H 1.8, N 14.9. ^1H NMR (200 MHz, $[D_6]DMSO$): δ = 8.52 (s, 1 H, H5); 7.99 (s, 1 H, H3); 3.88 (s, 3 H, CH_3) ppm.

Synthesis of $[Hg(1\text{-mtri})_2](ClO_4)_2$ (2): To a solution of 1-mtri (60.2 mg, 725 µmol) in H_2O (1 mL) was added an 83 mM solution of $Hg(ClO_4)_2$ in H_2O (5 mL). The suspension formed after about 1 h was stirred for 24 h at ambient temperature. The solid was collected by filtration, washed with cold H_2O (1 mL) and dried at 40 °C. Recrystallization from H_2O afforded **2** as colourless blocks (28.1 mg, 49.7 µmol, 7 %). ^1H NMR (200 MHz, $[D_6]DMSO$): δ = 9.17 (s, 1 H, H5); 8.50 (s, 1 H, H3); 4.09 (s, 3 H, CH_3) ppm.

Instrumentation: ^1H NMR spectra were recorded at T = 300 K with a Bruker Avance(II) 200 spectrometer. Chemical shifts were referenced to residual $[D_5]DMSO$ ($[D_6]DMSO$, δ = 2.50 ppm) or sodium 3-(trimethylsilyl)propanesulfonate (D_2O, δ = 0 ppm). Microanalyses were measured with a Leco CHNS 932 instrument.

Conditions for NMR Experiments: For the preparation of the Job plots, 20 mM solutions of ligand and metal salts [$AgClO_4$, $Hg(ClO_4)_2$] in D_2O were used. For the NMR titration, 10 mM solutions of ligand and 0.6 M solutions of the metal salts [$AgClO_4$, $Hg(ClO_4)_2$] in D_2O were used.

X-ray Crystallography: Crystal data were collected at 153(2) K with a Bruker APEX diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and were refined by full-matrix, least-squares on F^2 using the SHELXTL PLUS and SHELXL-97 programs.[19] All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were calculated on ideal positions. The perchlorate oxygen atoms were found to be disordered over two positions in compound **2**, with occupancy factors of 0.58 and 0.42. Relevant crystallographic data are listed in Table 4.

Table 4. Crystallographic data for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_3H_5AgClN_3O_4$	$C_6H_{10}Cl_2HgN_6O_8$
Formula weight	290.42	565.69
Crystal system	monoclinic	orthorhombic
Space group	*P*2/*c*	*Pbca*
a, *b*, *c* [Å]	11.4793(8), 9.4148(7), 7.1942(5)	7.200(2), 11.159(2), 18.081(4)
α, β, γ [°]	90, 99.189(1), 90	90, 90, 90
V [Å^3]	767.54(9)	1452.6(5)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	2.513	2.587
μ(Mo-K_α) [mm^{-1}]	2.952	11.017
Crystal size [mm]	0.02 × 0.05 × 0.34	0.09 × 0.20 × 0.23
θ_{min}, θ_{max} [°]	1.8, 31.9	2.3, 31.8
Data set	–16:16, –13:13, –10:10	–10:10, –16:16, –26:26
Total, unique data	9258, 2490	16515, 2390
Observed data [$I > 2\sigma(I)$]	2160	1720
N_{ref}, N_{par}	2490, 149	2390, 144
R, wR_2, S [$I > 2\sigma(I)$][a]	0.0303, 0.0799, 1.051	0.0254, 0.0719, 1.038
Min., max. resid. density [e Å^{-3}]	0.71, –1.65	0.89, –1.80

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

CCDC-775903 (for **1**) and CCDC-775904 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Complete Job plots and titration data.

Acknowledgments

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