Structural, Spectroscopic, and Reactivity Properties of N_2S_2(thioether)-O(amide)-Ligated Hg^{II} Complexes: The First Examples of Hg^{II}-Mediated Amide Cleavage

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Two mercury(II) complexes [(bmppa)Hg(ClO_4)]ClO_4 {**1**, bmppa = *N*,*N*-bis(2-methylthio)ethyl-*N*-[(6-pivaloylamido-2-pyridyl)methyl]amine} and [(beppa)Hg(ClO_4)]ClO_4 {**2**, beppa = *N*,*N*-bis(2-ethylthio)ethyl-*N*-[(6-pivaloylamido-2-pyridyl)-methyl]amine} of N_2S_2(thioether)O(amide)-donor chelate ligands have been prepared and characterized by X-ray crystallography and/or spectroscopic methods. In the solid state, the Hg^{II} ion of **2** exhibits an overall coordination number of six and strong amide oxygen coordination. Comprehensive multinuclear NMR studies of **1** and **2** have yielded the first $J_{^{199}Hg^{1}H}$ and $J_{^{199}Hg^{13}C}$ coupling constants associated with a Hg–$RSCH_3$ methyl group. In the presence of one equivalent of $Me_4NOH{\cdot}5H_2O$ in methanol/acetonitrile solution, the amide appendages of **1** and **2** undergo alcoholysis.

Introduction

The coordination chemistry of the Hg^{II} ion in biologically-relevant ligand environments is an area of current interest. For example, recent biochemical studies have focused on the use of ^{199}Hg NMR techniques in evaluating the active site coordination environments of Hg^{II}-substituted proteins.[1–2] ^{1}H NMR studies of Hg^{II} complexes of tripodal ligands have contributed to our understanding of the interplay of Hg^{II} coordination and spectroscopic properties by providing information regarding the magnitude of $J_{^{199}Hg^{1}H}$ and $J_{^{199}Hg^{13}C}$ coupling constants as a function of the nature of the Hg^{II} ligand environment.[3–7] Herein we outline the synthesis, structural and spectroscopic characterization, and amide cleavage properties of two Hg^{II} complexes of N_2S_2(thioether)O(amide)-donor chelate ligands. This work initiates advancement in two important areas of Hg^{II} coordination chemistry of relevance to biological systems. First, in seeking to expand the breadth of known spectroscopic features associated with Hg^{II} coordination, we have elucidated the first $J_{^{199}Hg^{1}H}$ and $J_{^{199}Hg^{13}C}$ coupling constants for Hg^{II}-$RSCH_3$ interactions. Second, we have commenced investigations into biologically-relevant reactions as a function of the group 12 metal ion present. In this context, we report herein that a Hg^{II} complex will mediate an amide cleavage reaction akin to that observed for zinc and cadmium analogs.[8] To the best of our knowledge, this work represents the first report in the chemical literature of Hg^{II}-mediated amide cleavage.

Results and Discussion

Preparation and Characterization of Hg^{II} Complexes

Mercury(II) complexes of the bmppa {*N*,*N*-bis(2-methylathio)ethyl-*N*-[(6-pivaloylamido-2-pyridyl)methyl] amine}and beppa {*N*,*N*-bis(2-ethylthio)ethyl-*N*-[(6-pivaloylamido-2-pyridyl)methyl]amine} ligands were prepared with $Hg(ClO_4)_2{\cdot}3H_2O$ in methanol (Scheme 1). Following crystallization from *i*PrOH/CH_3OH/Et_2O, [(bmppa) Hg(ClO_4)]ClO_4 (**1**) and [(beppa)Hg(ClO_4)]ClO_4 (**2**) were isolated in yields of 73% and 63%, respectively. Formulation of these complexes as having the amide oxygen coordinated to the Hg^{II} ion and one inner sphere perchlorate anion in the solid state is based on the X-ray crystal structure of **2** (vida infra) and the similarity of the solid state infrared spectral features for the amide moiety and perchlorate anions in **1** and **2**.

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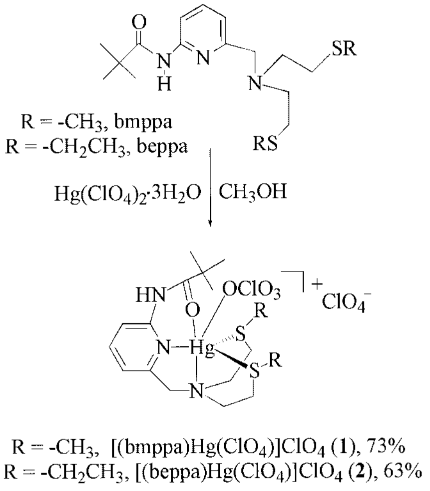


Scheme 1.

X-ray Crystallography

A summary of the X-ray data collection and refinement parameters for **2** is given in Table 1. An ORTEP representation of the cationic portion of **2** is shown in Figure 1. The Hg^{II} ion is well-known in two-coordinate linear or four-coordinate tetrahedral geometries.[9–13] However, the Hg^{II} center in **2** has an overall coordination number of six, with two short interactions involving the amide oxygen [Hg(1)–O(1) 2.271(5) Å; sum of Hg–O covalent radii 2.21 Å] and a thioether sulfur donor [Hg(1)–S(2) 2.4462(17) Å; sum of Hg–S covalent radii 2.50 Å][10] in a bent arrangement [O(1)–Hg(1)–S(2) 132.21(16)°]. As the Hg–O distance in **2** is only slightly longer than the sum of the covalent radii of the atoms, a strong interaction is present in the solid state for this complex. A search of the Cambridge Crystallographic Database revealed a complex of a 2-(pivaloylamido)-appended benzenethiolato ligand having a Hg–O (secondary amide) interaction akin to that in **2**.[14] However, the Hg–O distance in **2** is more than 0.5 Å shorter than the analogous bond length in bis[2,6-bis(pivaloylamido)benzenethiolato]mercury(II) [2.722(6) Å].[14] Typically, Hg^{II}–S(thioether) bond lengths are found in the range of 2.47–2.73 Å.[10–11,15–16] Thus, the Hg(1)–S(2) interaction is consistent with strong coordination to the Hg^{II} center, whereas the Hg(1)–S(1) bond length [2.6674(18) Å] indicates a weaker interaction. The remaining ligands to the Hg^{II} center of **2** are a pyridyl nitrogen [Hg(1)–N(2) 2.343(5) Å], a tertiary amine nitrogen [Hg(1)–N(3) 2.412(6) Å], and a weak Hg–O(perchlorate) interaction (3.01 Å). The $Hg–N_{py}$ and $Hg–N_{Am}$ distances in **2** are similar to the average corresponding distances found in $[(TMPA)HgCl]_2(HgCl_4)_2$ {$Hg–N_{py}$: 2.40 Å; $Hg–N_{am}$: 2.43 Å; TMPA = tris[(2-pyridyl)methyl]amine}.[3] Perchlorate coordination to Hg^{II} has been observed in several previously reported complexes.[4,17–21] In these, the Hg^{II}–O(perchlorate) bond lengths generally range from 2.66–2.95 Å. Notably, one of these reported structures has Hg^{II}–S(thioether) bonding as well as a weakly coordinated perchlorate (Hg–O, 3.08 Å) in a sixth coordination position.[18] Finally, key structural features of **2** are reminiscent of those found for the cadmium analog $[(bmppa)Cd(ClO_4)]ClO_4$.[8] Specifically, **2** and the Cd^{II} derivative both exhibit an overall six-coordinate distorted trigonal prismatic structure for the cation, with similar O(1)–M–N(2)–C(Ar) torsion angles {**2**: –13.8°; $[(bmppa)Cd(ClO_4)]ClO_4$: –22.5°} associated with coordination of the amide oxygen.

Table 1. Crystal data for **2**.[a]

	2
Empirical formula	$C_{19}H_{33}Cl_2HgN_3O_9S_2$
Formula mass	783.09
Crystal system	tetragonal
Space group	*I*-4*c*2
a [Å]	19.2193(2)
b [Å]	19.2193(2)
c [Å]	32.0617(5)
V [Å]	11843.0(3)
Z	16
Density (calcd.) [g cm^{-3}]	1.757
Temp. [K]	200(1)
Crystal size [mm]	0.27 × 0.18 × 0.12
Diffractometer	Nonius-Kappa CCD
Abs. coeff. [mm^{-1}]	5.568
$2\theta_{max}$ [°]	65.12
Reflection collected	16249
Independent reflections	9052[b]
Variable parameters	357
$R1$ [$I > 2\sigma I$]/w$R2$[c]	0.0419/0.0894
Goodness-of-fit (F^2)	1.013
Largest diff. peak [e·Å^{-3}]	0.746/–0.508

[a] Radiation used: Mo-$K\alpha$ (λ = 0.71073 Å). [b] All independent reflections were used in final refinement. [c] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)]/\Sigma[(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

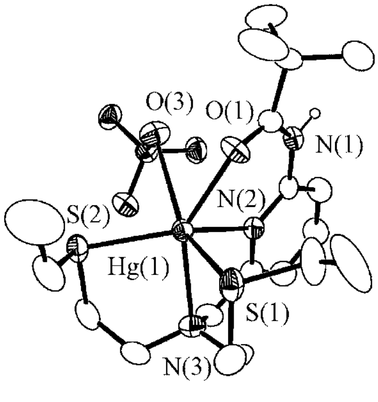


Figure 1. ORTEP representation of the cationic portion of **2**. Ellipsoids are plotted at the 30% probability level. Hydrogen atoms other than the amide N–H omitted for clarity; selected bond lengths [Å] and angles [°]: Hg(1)–O(1) 2.271(5), Hg(1)–S(1) 2.6674(18), Hg(1)–S(2) 2.4462(17), Hg(1)–N(2) 2.343(5), Hg(1)–N(3) 2.412(6), O(1)–Hg(1)–N(2) 79.02(17), N(2)–Hg(1)–S(1) 107.12(14), S(1)–Hg(1)–S(2) 112.27(6), N(2)–Hg(1)–S(2) 129.93(14).

Spectroscopic Properties of 1 and 2

Infrared Spectroscopy

In the solid state, **1** and **2** have amide carbonyl stretching vibrations at 1652 and 1647 cm^{-1}, respectively, a position that is ca. 36–41 cm^{-1} shifted from that observed for the free ligands (bmppa and beppa, $\nu_{C=O} \approx$ 1687 and 1688 cm^{-1}, respectively, neat between NaCl plates).[8,22] The reduced energy of the carbonyl vibrations in **1** and **2** is consistent with coordination to the Hg^{II} center. No significant difference is found in the solid state carbonyl stretching vibration as a function of metal ion, as zinc {[(beppa)Zn](ClO$_4$)$_2$, 1643 cm^{-1}} and cadmium analogs {[(bmppa)Cd(ClO$_4$)]ClO$_4$, 1654 cm^{-1}} have a $\nu_{C=O}$ vibration of similar energy.[8] The acetonitrile solution infrared spectrum of **1**, obtained in a new BaF$_2$ cell, exhibits a single $\nu_{C=O}$ vibration at 1647 cm^{-1}, indicating that amide oxygen coordination is maintained in solution. Notably, collection of a CH$_3$CN solution infrared spectrum of **1** in an older KBr cell yields a $\nu_{C=O}$ vibration at 1698 cm^{-1}. This higher energy $\nu_{C=O}$ vibration suggests that the amide oxygen is not coordinated to the Hg^{II} ion under these conditions. Since the solution infrared properties of **1** depend on the nature of the cell used for the infrared measurement, we currently hypothesize that the noncoordinated amide species formed in the KBr cell results from formation of a bromide derivative via anion exchange involving the cell salt.

NMR Spectroscopy

A wide array of 1D (^{1}H, ^{13}C, ^{199}Hg) and 2D ({^{1}H,^{1}H}COSY, {^{13}C,^{1}H}HMQC) NMR experiments have been used to characterize **1** (Figures S1–S3, Supporting Information) and **2** (Figures S4–S7) in acetonitrile solution. The cations of **1**, **2**, [(beppa)Zn](ClO$_4$)$_2$, [(bmppa)Zn](ClO$_4$)$_2$, and [(bmppa)Cd(ClO$_4$)]ClO$_4$ in acetonitrile solution, all exhibit *tert*-butyl methyl ^{1}H NMR resonances at a similar chemical shift (1.39–1.41 ppm).[8] Despite differences in the chemical environments of the sulfur alkyl substituents, and the differing Hg–S distances observed in the solid-state structure of **2**, a single sharp set of ^{1}H NMR resonances is observed for the S-C*H*$_3$ and -SC*H*$_2$C*H*$_3$ protons in CD$_3$CN solutions of **1** and **2** at ambient temperature. In this regard, we have previously noted a similar spectral appearance for the sulfur methyl protons in [(bmppa)Zn](ClO$_4$)$_2$.[8] In this complex, the thioether appendages undergo a rapid inversion process at room temperature (in CD$_3$OD solution) wherein the two possible directions of -SCH$_3$ canting (clockwise or counterclockwise) are rapidly interconverted via an intramolecular exchange process (coalescence temperature ca. –65 °C).[23]

A large heteronuclear coupling is evident in the -SC*H*$_3$ resonance of **1** [see Figure S1(b) in the Supporting Information, Table 2]. The intensities of the satellites ($\approx$ 17%) in this resonance are consistent with the natural abundance of ^{199}Hg (I = 1/2, 16.85%). To the best of our knowledge, this is the first reported $^3J_{^{199}Hg^1H}$ coupling involving a Hg-RSCH$_3$ methyl group.[10] Coupling between ^{199}Hg and methionine methyl protons has been previously detected indirectly for Hg^{II}-substituted plastocyanin.[1] The only other reported $J_{^{199}Hg^1H}$ values for Hg^{II} thioether complexes range from 36 to 90 Hz and involve methylene protons.[24,25] In nitrogen-only ligated Hg^{II} coordination complexes, a coupling constant of a similar magnitude (Table 2) has been previously reported for the benzylic -C*H*$_2$- resonance in the [Hg(TLA)]$^{2+}$ cation {TLA = tris[(6-methylpyrid-2-yl)methyl]amine}.[6] For the Cd^{II} analog [(bmppa)Cd(ClO$_4$)]ClO$_4$, the $J_{^{111/113}Cd^1H}$ coupling constant in the Cd^{II}-RSCH$_3$ thioether methyl resonance is much smaller.[8,26]

Table 2. Heavy atom/proton coupling constants ($J_{^{199}Hg^1H}$ or $J_{^{111/113}Cd^1H}$) identified in the ^{1}H NMR spectra of **1**, **2**, and structurally related complexes.

Complex	*H*	*J* [Hz]	Ref.
[(bmppa)Hg(ClO$_4$)]ClO$_4$ (**1**)[a]	-SC*H*$_3$	91	this work
	benzylic -C*H*$_2$-	27	
[(beppa)Hg(ClO$_4$)]ClO$_4$ (**2**)[a]	benzylic -C*H*$_2$-	26	this work
[Hg(TLA)](ClO$_4$)$_2$	benzylic -C*H*$_2$-	72	[6]
[(TMPA)Hg](ClO$_4$)$_2$	benzylic -C*H*$_2$-	36	[3]
[(TMPA)HgCl]Cl	benzylic -C*H*$_2$-	45	[3]
[(bmppa)Cd(ClO$_4$)]ClO$_4$[b]	-SC*H*$_3$	15	[8]
	benzylic -C*H*$_2$-	9.6	

[a] Spectra recorded in dry CD$_3$CN at 25(1) °C on a Bruker ARX-400. [b] JEOL 270 MHz spectrometer.

For both **1** and **2**, benzylic -C*H*$_2$- resonances having ^{199}Hg coupling satellites are identifiable in the ^{1}H NMR spectra of the complexes [Table 2; Figures S1(a) and S4(a)]. These $^{3/4}J_{^{199}Hg^1H}$coupling constants are slightly smaller than those observed in the benzylic proton resonances of [(TMPA)Hg](ClO$_4$)$_2$ {TMPA = tris[(2-pyridyl)methyl]amine} and [(TMPA)HgCl]Cl, but are significantly larger than the $^{3/4}J_{^{111/113}Cd^1H}$ coupling constant found in benzylic -C*H*$_2$- resonance of [(bmppa)Cd(ClO$_4$)]ClO$_4$.[3,8]

The -S*C*H$_3$ resonance in the ^{13}C{^{1}H} NMR spectrum of **1** exhibits two-bond $_{^{199}Hg^{13}C}$ coupling [Table 3, Figure S2(f)] as does the -S*C*H$_2$CH$_3$ methylene carbon resonance of **2** [Figure S5(e2)]. This methylene carbon resonance was assigned via {^{13}C,^{1}H}HMQC (Figure S7). For each complex the methylene linker carbons of the thioether arms exhibit $^{2/3}J_{^{199}Hg^{13}C}$ coupling [Figures S2(d) and (e); Figures S5(d) and (e1)]. Notably, the methylene C signal found at ca. 48.4–48.6 ppm in **1** and **2** exhibits a much larger $^{2/3}J_{^{199}Hg^{13}C}$coupling constant than that found for the other methylene linker C atom at about 32–35 ppm (Table 3). Conclusive identification of which of these resonances represents the carbon adjacent to the sulfur donor in the linker arms of each complex has not yet been accomplished.

Finally, ^{199}Hg heteronuclear coupling is found in two pyridyl ring carbon resonances in **1** and **2**. Specifically, an *ortho*-carbon resonance at δ = 153.7 ppm for each complex (Table 3) has a larger coupling constant than a *meta* ring carbon resonance at ~124 ppm. The assignment of these resonances as *ortho*- and *meta*-carbons was achieved via {^{13}C,^{1}H}HMQC experiments for both complexes.

As **1** and **2** exhibit generally similar solution NMR properties, we examined only **2** via ^{199}Hg NMR spectroscopy. For this complex, a single resonance is found at –1124 ppm, as referenced to an external standard of phenylmercuric acetate in DMSO (–1439.5 ppm). Whereas thiolate-ligated Hg^{II} centers tend to have ^{199}Hg NMR resonances in the region of –100 to –400 ppm, the ^{199}Hg chemical shift found

Table 3. Heteroatom coupling constants ($J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$) observed in the $^{13}C\{^1H\}$ NMR spectra of **1** and **2**.

Complex	C	J [Hz]
[(bmppa)Hg(ClO_4)]ClO_4 (**1**)	-S*C*H_3	36
	-N*C*H_2*C*H_2S-[b]	75, 14
	benzylic -*C*H_2-	20
	o-*C*$_6$$H_4$N	35
	m-*C*$_6$$H_4$N	17
[(beppa)Hg(ClO_4)]ClO_4 (**2**)	-SCH_2*C*H_3	46
	-S*C*$H_2$$CH_3$	32
	-N*C*H_2*C*H_2S-[b]	73, 15
	benzylic -*C*H_2-	19
	o-*C*$_6$$H_4$N	33
	m-*C*$_6$$H_4$N	16

[a] Spectra recorded in dry CD_3CN at 25(1) °C on a Bruker ARX-400. [b] Methylene carbon resonances were not individually assigned.

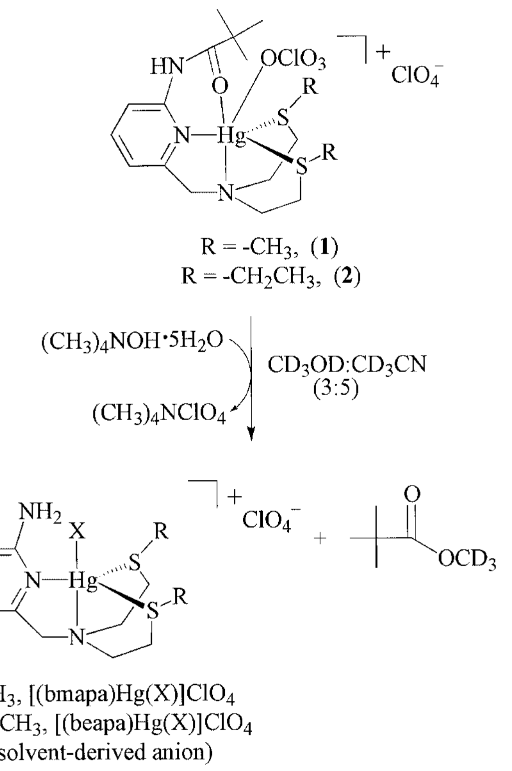
for **2** is similar to that found for all nitrogen-ligated Hg^{II} complexes (–1200 to –1400 ppm).[1] A comparable result was recently identified for N_2S_2(thioether)-ligated Cd^{II} complexes.[27]

These combined infrared and NMR studies indicate that the nitrogen and sulfur donors of the bmppa and beppa chelate ligands, as well as the amide oxygen, are coordinated to the Hg^{II} centers of **1** and **2** in acetonitrile solution.

Amide Cleavage Reactivity

Reaction of **1** with an equimolar amount of $Me_4NOH{\cdot}5H_2O$ in CD_3OD/CD_3CN solution (3:5) at 55(1) °C results in amide alcoholysis of the *tert*-butyl amide moiety to quantitatively yield [D_3]methyl trimethylacetate and a Hg^{II} complex of a primary amine-appended chelate ligand (Scheme 2).

The ester product was identified by ^1H NMR [δ = 1.18 ppm (s, 9 H)] via spectral comparison to an authentic sample of methyl trimethylacetate (Aldrich).[8] One equivalent of Me_4NClO_4 is produced in the amide cleavage reaction of **1** and has been isolated from the reaction mixture in 81% yield as described for the similar amide methanolysis reaction of [(bmppa)Zn]$(ClO_4)_2$.[8] The Hg^{II} product of the amide cleavage reaction of **1** could not be isolated cleanly. This is probably due to the fact that the complex will have one solvent derived anion (OH^- or OCD_3^- or a mixture of both). However, the formation of bmapa-ligand Hg^{II} products is apparent from the ^1H NMR features of the final reaction mixture. Specifically, the signals associated with the *meta*-protons of the primary amine-appended pyridyl donor in the bmapa-ligated product resonate significantly upfield (6.63 and 6.85 ppm) of the same protons in **1**. This is consistent with the chemical transformation from an electron-withdrawing amide group to the electron-donating primary amine substituent on the pyridyl ring. A similar final reaction mixture is obtained following treatment of **2** with $Me_4NOH{\cdot}5H_2O$ in CD_3OD/CD_3CN solution (3:5) at 55(1) °C. Notably, exposure of the free bmppa or beppa ligand to $Me_4NOH{\cdot}5H_2O$ in CD_3OD/CD_3CN solution (3:5) at 55(1) °C does not result in signficant amide cleavage (< 1%) in the time required for complete amide cleavage in **1**, **2**, or the zinc and cadmium analogs that have been previously reported.[8] Further investigations are directed at elucidation of the mechanism of amide cleavage in these systems.



Scheme 2.

Conclusions

The synthesis and structural characterization of two new Hg^{II} complexes of N_2S_2(thioether)O(amide) donor chelate ligands has been accomplished. Comprehensive solution infrared and NMR studies of these complexes has revealed that strong N_2S_2 and amide oxygen coordination are maintained in CH_3CN solution. Using these complexes, heteronuclear coupling constants ($J_{^{199}\mathrm{Hg}^{1}\mathrm{H}}$and $J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$) for Hg^{II}–S(thioether) interactions have been determined. Particularly notable is the identification of a large $^3J_{^{199}\mathrm{Hg}^{1}\mathrm{H}}$ coupling constant (91 Hz) observed in the methyl proton resonance of a Hg^{II}-$RSCH_3$ interaction. Treatment of these amide-appended Hg^{II} derivatives with $Me_4NOH{\cdot}5H_2O$ in methanol/acetonitrile solution has provided the first examples of Hg^{II}-mediated amide cleavage.

Experimental Section

General Remarks: Reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. FTIR spectra were recorded on a Shimadzu FTIR-8400 spectrometer as KBr pellets or CH_3CN solutions between BaF_2

or KBr plates. ^{1}H, ^{13}C{^{1}H}, {^{1}H,^{1}H}COSY, and {^{13}C,^{1}H}HMQC NMR spectra were recorded in dry CD_3CN at 25(1) °C on a Bruker ARX-400 spectrometer. Chemical shifts (in ppm) are referenced to the residual solvent peaks in CD_3CN (^{1}H: 1.94 (quintet); ^{13}C{^{1}H}: 1.39 (heptet) ppm). ^{199}Hg NMR spectra were recorded at 71.6 MHz on a Varian Mercury VX NMR spectrometer with CH_3CN as the solvent, at concentrations of about 112 mM and about 30 mM. These spectra were referenced to an external standard of 0.5 M phenylmercuric acetate in DMSO (–1439.5 ppm). Fast atom bombardment (FAB) mass spectra were collected at the University of California, Riverside using a VG ZAB2SE high resolution mass spectrometer in a matrix of *m*-nitrobenzylalcohol (NBA). The chelate ligands bmppa and beppa were prepared as previously reported.[8,22]

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. These compounds should be handled in small amounts and should be treated with extreme caution, especially in the solid state.[28]

[(bmppa)Hg(ClO$_4$)]ClO$_4$ (1): Prepared in an identical manner to [(bmppa)Zn](ClO$_4$)$_2$.[8] Recrystallization of a white powder by diethyl ether diffusion into a *i*PrOH/CH_3OH, 1:1 solution yielded colorless blocks (94 mg, 73%). ^{1}H NMR [CD_3CN, 400 MHz, 25(1) °C]: δ = 1.39 (s, 9 H), 2.34 (t, $^{3}J_{^{199}\mathrm{Hg}^{1}\mathrm{H}}$ = 91 Hz, 6 H), 2.95–3.50 (m, 8 H), 4.01 (t, $^{3/4}J_{^{199}\mathrm{Hg}^{1}\mathrm{H}}$ = 27 Hz, 2 H), 7.36 (d, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 1 H), 7.42 (d, $^{3}J_{\mathrm{H,H}}$ = 8.1 Hz, 1 H), 8.04 (t, $^{3}J_{\mathrm{H,H}}$ = 7.9 Hz, 1 H), 9.04 (br. s, 1 H, N-*H*) ppm; ^{13}C{^{1}H} NMR [CD_3CN, 100 MHz, 25(1) °C]: δ = 18.0 (t, $^{2}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 36 Hz), 27.4, 34.2 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 14 Hz), 42.7, 48.4 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 75 Hz), 56.8 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 20 Hz), 118.6, 123.9 (t, $^{3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 17 Hz), 143.6, 153.7 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 35 Hz), 154.6, 186.4 (12 signals expected and observed). FTIR (KBr, cm^{-1}): 3337 (br., $\nu_{\mathrm{N-H}}$), 1652 ($\nu_{\mathrm{C=O}}$), 1613, 1529, 1092 (ν_{ClO4}), 623 (ν_{ClO4}). FTIR (CH_3CN, BaF_2 cell, cm^{-1}): 1647 ($\nu_{\mathrm{C=O}}$). LRFAB-MS (CH_3CN/NBA), *m*/*z* (%): 656 [M – ClO$_4$]$^+$ (60%). $C_{17}H_{29}Cl_2HgN_3O_9S_2$ (755.05): calcd. C 27.02, H 3.87, N 5.56; found: C 27.07, H 3.88, N 5.57.

[(beppa)Hg(ClO$_4$)]ClO$_4$ (2): Prepared in an identical manner to [(beppa)Zn](ClO$_4$)$_2$.[8] Recrystallization of a white powder by diethyl ether diffusion into a *i*PrOH/CH_3OH, 1:1 solution yielded colorless prisms suitable for X-ray diffraction analysis (81 mg, 63%). ^{1}H NMR [CD_3CN, 400 MHz, 25(1) °C]: δ = 1.33 (t, $^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 6 H), 1.39 (s, 9 H), 2.50–2.90 (m, 4 H), 2.97–3.45 (m, 8 H), 4.02 (t, $^{3/4}J_{^{199}\mathrm{Hg}^{1}\mathrm{H}}$ = 26 Hz, 2 H), 7.37 (d, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 1 H), 7.44 (d, $^{3}J_{\mathrm{H,H}}$ = 8.2 Hz, 1 H), 8.04 (t, $^{3}J_{\mathrm{H,H}}$ = 7.9 Hz, 1 H), 9.09 (br., 1 H, N-*H*) ppm; ^{13}C{^{1}H} NMR [CD_3CN, 100 MHz, 25(1) °C]: δ = 14.1 (t, $^{3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 46 Hz), 27.4, 30.2 (t, $^{2}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 32 Hz), 32.0 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 15 Hz), 42.7, 49.2 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 73 Hz), 56.9 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 19 Hz), 118.5, 124.0 (t, $^{3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 16 Hz), 143.6, 153.7 (t, $^{2/3}J_{^{199}\mathrm{Hg}^{13}\mathrm{C}}$ = 33 Hz), 154.7, 186.5 ppm (13 signals expected and observed). ^{199}Hg NMR (CH_3CN, 71.6 MHz) –1124 ppm. FTIR (KBr, cm^{-1}): 3347 (br., $\nu_{\mathrm{N-H}}$), 1647 ($\nu_{\mathrm{C=O}}$), 1616, 1580, 1533, 1098 (ν_{ClO4}), 625 (ν_{ClO4}); LRFAB-MS (CH_3CN/NBA), *m*/*z* (%): 684 [M – ClO$_4$]$^+$ (60%), 584 [M – 2ClO$_4$–CH_3CN+H]$^+$ (100%). $C_{19}H_{33}Cl_2HgN_3O_9S_2$ (783.10): calcd. C 29.12, H 4.25, N, 5.36; found: C 29.31, H 4.30, N 5.30.

^{1}H-NMR Analysis of Amide Cleavage Reactions of Amide-Appended Hg^{II} Complexes: To a solution of **1** (14.0 mg, 0.019 mmol) in CD_3CN/CD_3OD (500 µL:300 µL) solution was added $(CH_3)_4NOH{\cdot}5H_2O$ (3.4 mg, 0.019 mmol) and an internal standard ($CHPh_3$, 4.5 mg, 0.019 mmol). The resulting mixture was monitored by ^{1}H NMR at 55(1) °C at two-minute intervals for 50 minutes at which point the reaction had reached completion, as indicated by the formation of one equivalent of $(CH_3)_3C(O)OCD_3$. The formation of a bmapa-ligated {bmapa = *N*,*N*-bis(2-methylthio)ethyl-*N*-[(6-amino-2-pyridyl)methyl]amine} Hg^{II} product is indicated by the appearance of two upfield-shifted pyridyl ring doublets at δ = 6.63 and 6.85 ppm, respectively {[(bmapa)HgX]ClO$_4$ (X = -OH or -OCD$_3$): ^{1}H NMR [CD_3CN, 270 MHz, 22(1) °C]: δ = 1.98 (s, 6 H), 2.82–3.25 (m, 8 H), 3.81 (s, 2 H), 6.63 (d, $^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 1 H), 6.85 (d, $^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 1 H), 7.50–7.55 (m, 1 H) ppm}. This result is very similar to that observed for the amide cleavage reaction of [(bmppa)Zn](ClO$_4$)$_2$, wherein the bmapa ligand has been removed and comprehensively characterized.[8] The reaction of **2** with $(CH_3)_4NOH{\cdot}5H_2O$ under identical conditions proceeds in a similar fashion to give a beapa-ligated {beapa = *N*,*N*-bis(2-ethylthio)ethyl-*N*-[(6-amino-2-pyridyl)methyl]amine[8]} Hg^{II} complex {[(beapa)HgX]ClO$_4$ (X = -OH or -OCD$_3$): ^{1}H NMR [CD_3CN, 400 MHz, 25(1) °C]: δ = 1.11 (t, $^{3}J_{\mathrm{H,H}}$ = 7.4 Hz, 6 H), 2.32–2.40 (m, 4 H), 2.80–2.95 (m, 6 H), 3.15–3.22 (m, 2 H), 3.70 (t, $^{3}J_{^{199}\mathrm{Hg}^{1}\mathrm{H}}$ = 22 Hz, 2 H), 6.62 (d, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz, 1 H), 6.84 (d, $^{3}J_{\mathrm{H,H}}$ = 8.5 Hz, 1 H), 7.50–7.55 (m, 1 H) ppm} and $(CH_3)_3C(O)OCD_3$.

Identification and Quantification of [D$_3$]Methyl Trimethylacetate Produced in Amide Alcoholysis Reactions of 1 and 2: Methyl trimethylacetate formation was identified and quantified by ^{1}H NMR as described previously.[8]

Identification and Quantification of $(CH_3)_4NClO_4$in a Hg^{II}-Mediated Amide Cleavage Reaction: To a solution of **2** (33.4 mg, 4.26×10^{-2} mmol) in methanol (or methanol/acetonitrile) solution (≈ 3 mL) was added $(CH_3)_4NOH{\cdot}5H_2O$ (7.7 mg, 4.25×10^{-2} mmol). The resulting mixture was stirred for ca. 1 minute during which time a white precipitate appeared. The solution was then carefully decanted from the white solid, which was subsequently dried (6.0 mg, 81%) and identified as $(CH_3)_4NClO_4$ by infrared spectroscopy.

X-ray Structure Determination of 2: A colorless prism shaped crystal of **2** was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius-KappaCCD diffractometer equipped with Mo-*K*α radiation for data collection. Ten frames of data were collected at 200(1) K with an oscillation range of 1 deg/frame and an exposure time of 20 sec/frame. Indexing and unit cell refinement based on all observed reflections from those ten frames indicated a tetragonal *I* lattice. A total of 16249 reflections were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPACK.[29] The structure was solved by a combination of direct and heavy atom methods using SIR 97.[30] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients *U*(H) = 1.2 *U*(C) or 1.5 *U*(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[31] Oxygen atoms of one perchlorate anion were found to exhibit disorder. These oxygen atoms were each split into two fragments [O(6)/O(6′), O(7)/O(7′), O(8)/O(8′), and O(9)/O(9′)] and refined. This refinement led to a 0.51:0.49 ratio in occupancy over two positions for each oxygen atom. Further details of the X-ray data collection and refinement of [(beppa)Hg(ClO$_4$)]ClO$_4$ (**2**) are given in Table 1. CCDC-249460 contains 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 footnote on the first page of this article): Contains figures developed from the 1D and 2D NMR spectra of **1** and **2**.

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