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Article

Preparation and Comprehensive Characterization of $[Hg_6(Alanine)_4(NO_3)_4] \cdot H_2O$

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A new mercury−alanine complex has been isolated from reaction mixtures of mercurous nitrate dihydrate and alanine (L and D enantiomers). The solid-state structure contains mercury(I) and mercury(II) associated by alanine ligands in a polymeric array. The disproportionation of mercury(I) to mercury(II) and mercury(0) was facilitated by alanine and is evidenced by the appearance of mercury(0) in reactions of mercury(I) with the 20 common amino acids. This complex is the first mercury(I)−amino acid complex characterized in the solid state. The compounds have been comprehensively characterized using X-ray crystallography, solid-state and solution-state nuclear magnetic resonance spectroscopy, vibrational spectroscopies, and electrospray ionization mass spectrometry.

Introduction

The toxic effects of mercury poisoning are extensively documented.[1,2] For example, the neurological symptoms of Minamata disease are evident in populations in which a major food source has been contaminated by methylmercury.[3] However, the chemical interactions that occur between biological molecules and mercury are not well understood. Although ions of heavy metals potentially interact with many bioligands, complexes formed between heavy metals and amino acids, peptides, or proteins likely have the most dramatic physiological consequences. Some complexes containing organic or inorganic mercury(II) with amino acid ligands have been crystallographically characterized (amino acid = alanine[4,5] (ala), cysteine,[6,7] glycine,[4] histidine,[8] methionine,[9–11] proline,[12] serine,[13] tryptophan,[14,15] tyrosine,[16] N-acetyltryptophan,[15] 2-amino-4-phenylbutanoic acid,[16] ethionine,[17] homocysteine,[14] S-methyl-cysteine,[9,17] penicillamine,[10,18–20] and the dipeptide glycylglycine[21]), yet the available data are often specific to an isolated crystal and may or may not be relevant to the solution behavior of the compound. In addition, limited characterization data are available, precluding meaningful comparisons and the development of a self-consistent model for the interaction of mercury with amino acids.

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Table 1. Crystallographic Data for $[Hg_{12}(\text{L-ala})_8(NO_3)_8]\cdot 2H_2O$ and $[Hg_{12}(\text{D-ala})_8(NO_3)_8]\cdot 2H_2O$

	$[Hg_{12}(\text{L-ala})_8(NO_3)_8]\cdot 2H_2O$	$[Hg_{12}(\text{D-ala})_8(NO_3)_8]\cdot 2H_2O$
empirical formula	$C_{24}H_{52}Hg_{12}N_{16}O_{42}$	$C_{24}H_{52}Hg_{12}N_{16}O_{42}$
fw	3643.90	3643.90
cryst dimensions	0.36 × 0.22 × 0.06	0.43 × 0.09 × 0.05
cryst syst	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a (Å)	10.6210(11)	10.6255(6)
b (Å)	19.7259(19)	19.7285(11)
c (Å)	15.3150(15)	15.3184(9)
β (deg)	91.5646(14)	91.5655(8)
V (Å^3)	3207.4(6)	3209.9(3)
Z	2	2
ρ_{calcd} (g cm^{-3})	3.773	3.770
μ (mm^{-1})	28.708	28.685
2θ (deg)	52.80	54.54
total number of data collected	22560	28120
	$-13 \le h \le 13$	$-13 \le h \le 13$
	$-24 \le k \le 24$	$-25 \le k \le 25$
	$-19 \le l \le 19$	$-19 \le l \le 19$
number of independent reflns	12859	14518
R_{int}	0.0367	0.0308
number of observed reflns	11021	13213
range of transmission factors	0.2777–0.0344	0.3281–0.0285
number of data/restraints/params	12859/859/11	14518/859/11
Flack absolute structure parameter	−0.015(11)	−0.005(7)
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0481	0.0280
wR_2 [$F_o^2 \ge 3\sigma(F_o^2)$]	0.0844	0.0569
GOF	1.043	1.001

Herein, we describe the preparation, isolation, and comprehensive study of two enantiomers of a new mercury−alanine complex, including characterization by means of X-ray crystallography, nuclear magnetic resonance (NMR) spectroscopy, IR spectroscopy, Raman spectroscopy, and electrospray ionization mass spectrometry (ESI-MS). The compound is a unique example of an amino acid complex containing both mercury(I) and mercury(II) metal centers, enabling a direct structural and spectroscopic comparison of both coordination environments.

Experimental Section

Caution! *Compounds of mercury are highly toxic.*[22] *Care must be taken when handling samples, and appropriate disposal procedures are necessary.*

General. Mercury(I) nitrate dihydrate, L-alanine, and D-alanine were used as received from Sigma-Aldrich. Distilled water was used in all crystallization procedures, and all procedures were carried out in the air, unless otherwise indicated.

Preparation and Isolation of $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$. A stirred solution (10 min) of L-alanine (5.04×10^{-3} mol) in 10 mL of distilled water (pH 6.4) was added to a suspension of $Hg_2(NO_3)_2\cdot 2H_2O$ (2.51×10^{-3} mol) in 30 mL of distilled water (stirred 10 min), resulting in a white cloudy suspension with a pH of 1.8. The mixture was heated at 90 °C for 20 min, and the solution became clear and colorless with the precipitation of elemental mercury. The hot solution was suction-filtered and slowly cooled to room temperature. Yellow needlelike crystals of $[Hg_{12}(\text{L-ala})_8(NO_3)_8]\cdot 2H_2O$ (**L**) formed from the filtrate in 30 days at room temperature. Yield: 0.201 g, 17.6%. mp: 150 °C. d.p.: 160 °C. Elem anal. for $C_{24}H_{52}Hg_{12}N_{16}O_{42}$, 3643.90 g mol^{-1}, exptl (calcd): %C 8.83 (7.89), %H 1.70 (1.66), %N 6.62 (6.14). This procedure was also altered to decrease the crystallization time; the hot filtered solution was evaporated at its boiling point to approximately half of the original volume and then left open to the air to cool slowly; after 13 days, the yield was 30.2%.

The procedure above was applied using D-alanine (5.04×10^{-3} mol) in 10 mL of distilled water (pH 6.4) and using $Hg_2(NO_3)_2\cdot 2H_2O$ (2.51×10^{-3} mol) in 30 mL of distilled water (white cloudy suspension, pH 2.2) and yielded yellow needlelike crystals of $[Hg_{12}(\text{D-ala})_8(NO_3)_8]\cdot 2H_2O$ (**D**) after 3 weeks of slow evaporation at room temperature. Yield: 18.4%. mp: 152 °C. d.p.: 162 °C.

Attempts to isolate solids from reaction mixtures of mercurous nitrate with an equimolar mixture of L- and D-alanine gave a slightly yellow, viscous oil.

The procedure was applied for the 20 common amino acids with mercurous nitrate. Crystals were only produced with alanine; however, mercury(0) was observed in reactions containing alanine, arginine, asparagine, glutamic acid, glutamine, glycine, proline, serine, and threonine. Reactions of mercurous nitrate with asparagine, cysteine, histidine, lysine, methionine, phenylalanine, tryptophan, and tyrosine produced dark gray precipitates, and white precipitates resulted from the isoleucine, leucine, and valine reactions.

X-Ray Crystallography. Crystals of $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$ were coated in Paratone-N oil and then mounted on a thin glass fiber and cooled to 193(2) K under a cold N_2 stream. X-ray diffraction data were obtained using a Bruker PLATFORM diffractometer with a SMART 1000 CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Programs for diffractometer operation, unit cell indexing, data collection, data reduction, and absorption correction were supplied by Bruker. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the Patterson search/structure expansion facilities within the *DIRDIF-*

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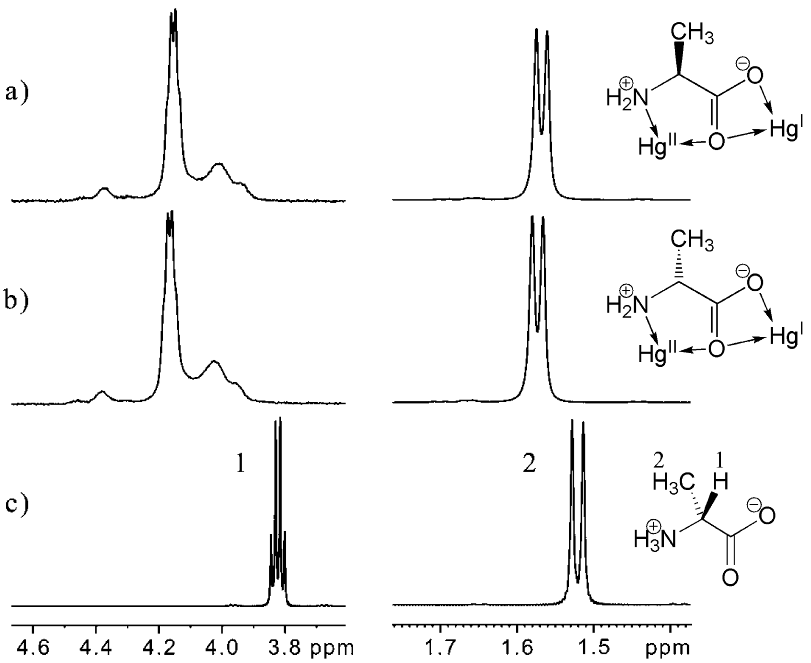

Figure 1. Solution-state ^1H NMR of (a) [Hg_{12}(L-ala)$_8$(NO_3)$_8$]·$2H_2O$ crystals (<0.0026 M), (b) [Hg_{12}(D-ala)$_8$(NO_3)$_8$]·$2H_2O$ crystals (<0.0026 M), and (c) D-alanine dissolved in deuterium oxide. The methyl and methine peaks are not normalized.

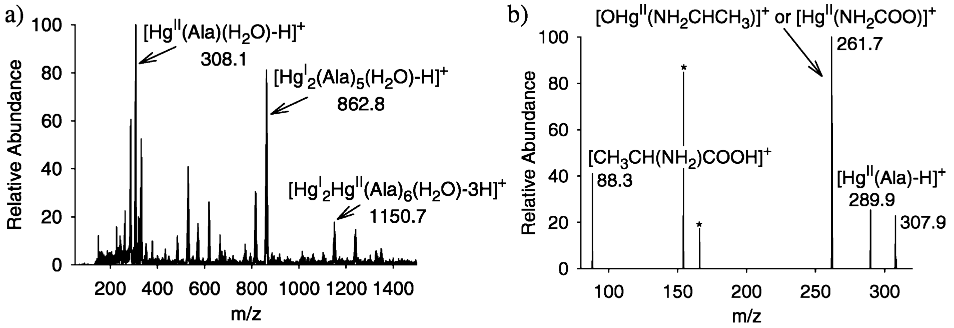

Figure 2. (a) Positive ion ESI mass spectrum of a reaction mixture containing $Hg_2(NO_3)_2$·$2H_2O$ with L-alanine in 50:50 methanol/water. (b) Tandem mass spectrum of *m/z* 308 at 20% collision energy; peaks indicated with an asterisk are not fragments of a mercury-containing complex cation.

99 program system.[23] Refinements were completed using the program *SHELXL-97*.[24] Hydrogen atoms were assigned positions on the basis of the geometries of their attached carbon, nitrogen, or oxygen atoms and were given thermal parameters 20% (for C−H or N−H) or 50% (for O−H) greater than those of their parent atoms. For both structures, an idealized geometry was imposed upon the water molecules by fixing the O−H bond distances at 1.00 Å and the intramolecular H···H distances at 1.63 Å during refinement. These water hydrogen atoms were oriented toward nearby nitrate group oxygen atoms by constraining the four atoms of the O–H···O–N hydrogen-bonded units to be coplanar (i.e., by setting these atoms to define a tetrahedron with a volume of no more than 0.001 Å^3). See Table 1 for a summary of crystal parameters.

Solid-State ^{13}C NMR Spectroscopy. Samples for solid-state ^{13}C NMR spectroscopy were ground into a fine powder and packed into a 4 mm rotor. All experiments were carried out on a Bruker Avance NMR spectrometer with a 9.4 T magnet (400 MHz proton Larmor frequency, 100.65 MHz ^{13}C Larmor frequency) using a double-resonance probe head for rotors of 4 mm diameter. The sample was spun at 8.0 and 10.0 kHz to determine center bands and to identify spinning sidebands. Relaxation times for the protons were determined by inversion–recovery sequences. From these experiments, a recycle delay of 10.00 s was employed for the ^{13}C cross-polarization (CP)/magic angle spinning (MAS) determination. The other parameters for the ^{13}C CP/MAS experiments with two-pulse phase modulation proton decoupling were optimized on glycine, whose carbonyl resonance also served as an external, secondary chemical shift standard at 175.06 ppm. For the ^{13}C CP/MAS NMR spectra, 16 scans were accumulated, using 2.6 ms CP contact times.

Solution-State ^{1}H NMR Spectroscopy. Solution ^{1}H NMR spectra were obtained using a Bruker Avance NMR spectrometer with a 11.74 T magnet (500 MHz proton Larmor frequency, 125.81 MHz ^{13}C Larmor frequency). Crystals of [Hg_{12}(L-ala)$_8$(NO_3)$_8$]·$2H_2O$ or [Hg_{12}(D-ala)$_8$(NO_3)$_8$]·$2H_2O$ were dissolved in deuterium oxide. Samples were sonicated for 10 min and centrifuged for 2 min at 10 000 rpm to separate any precipitate. ^{1}H NMR methine signals were observed at 4.15 ppm ($^3J_{HH}$ 7.0 Hz) and 4.00 ppm (broad) for [Hg_{12}(L-alanine)$_8$(NO_3)$_8$]·$2H_2O$ crystals and 4.17 ppm ($^3J_{HH}$ 7.0 Hz) and 4.02 ppm for [Hg_{12}(D-alanine)$_8$(NO_3)$_8$]·$2H_2O$ crystals, while the methyl signals were observed at

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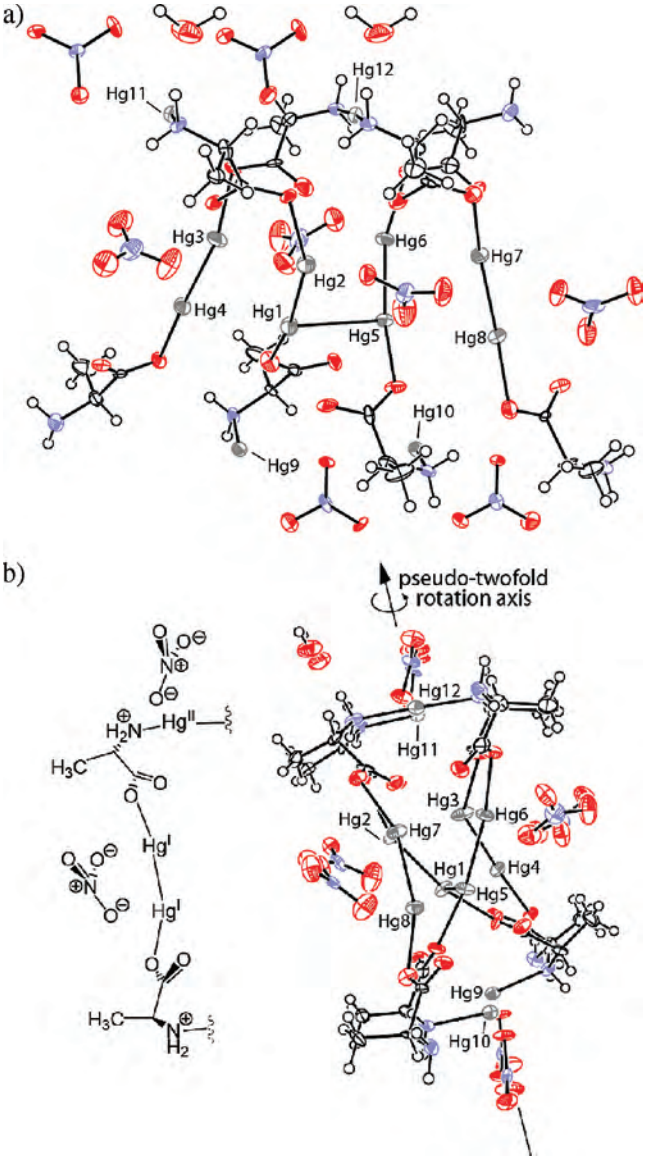

Figure 3. Asymmetric unit of $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ with calculated positions for hydrogen atoms, (a) viewed along the crystal *b* axis and (b) viewed along the crystal *a* axis—for clarity, only the shortest covalent bonds are indicated. The diagram on the left in b shows the connectivity of the monomeric unit. Thermal ellipsoids are shown at 50% probability, except for the hydrogen atoms, which are shown as small spheres of arbitrary size.

1.57 ppm ($^3J_{HH}$ 7.0 Hz) for both crystals (Figure 1). Mercury−D-alanine reaction mixtures were prepared for NMR analysis by following the sample preparation procedure using deuterium oxide rather than distilled water and were heated under $N_{2(g)}$. Attempts to obtain solution ^{13}C NMR data on solutions in deuterium oxide were not successful (saturated solution in distilled water, 0.0026 M, after overnight mixing). All attempts to obtain solution ^{199}Hg NMR spectra on solutions of the reaction mixtures in deuterium oxide were also unsuccessful.

Electrospray Ionization Mass Spectroscopy (ESI-MS). Electrospray ionization mass spectra were obtained on aliquots of the hot filtrates that were subsequently diluted in distilled water and also in 50/50 (v/v) methanol/distilled water (final concentration 1.25 × 10^{-2} M). Positive and negative ion ESI-MS spectra were obtained using a Finnigan LCQ DUO ion trap mass spectrometer. Two separate flow solvents were used, distilled water and 50/50 (v/v) methanol/distilled water. Instrument parameters were set at 1.2 mL/h for the flow solvent rate, 4.00 kV for the spray voltage, and 200 °C for the capillary temperature, and the in-source fragmentation option was not activated. The relative abundance of each peak for each sample type was reproducible within the ranges H (75−100%), M (35−75%), or L (3−35%). To verify the ion identity for each spectral peak, the experimentally observed isotope peak patterns of *m*/*z* 308, 863, and 1151 were compared to calculated isotope patterns using Isotope Pattern Calculator v 4.0,[25] see the Supporting Information. In addition, tandem mass spectrometric analysis of the ion represented by *m*/*z* 308 was also performed (Figure 2b and the Supporting Information). All spectra were analyzed and processed using Qual Browser,[26] Microsoft Excel 2002,[27] and Sigma Plot.[28]

Vibrational Spectroscopy. Samples for IR spectroscopy were prepared as Nujol mulls between CsI disks. Samples for Raman spectroscopy were ground into fine powders and packed into glass capillary tubes. Raman and IR data, presented in the Supporting Information, were collected on a Bruker RFS 100 FT-Raman Spectrometer (Nd:YAG laser, emission wavelength 1.06 μm, output power 80 mW) and a Bruker Vector 22 spectrometer (He:Ne laser, emission wavelength 633 nm, output power 1 mW), respectively. Peak assignments are based on those proposed for methylmercury-L-alanine as well as other mercury−amino acid compounds,[5,6,29,30] and the mercury−mercury peak assignment was based upon a mercury(I) solvation study.[31]

pH measurements were performed using a ROSS Sure-Flow combination pH electrode with a ThermoOrion model 230 pH meter. Elemental analysis was performed by Canadian Microanalytical Service Ltd., in British Columbia, Canada.

Results and Discussion

As part of a systematic assessment of the coordination complexes that form between heavy metals and amino acids,[32–40] we have established appropriate conditions for the crystallization of an enantiomeric pair of mercury−alanine complexes. Heated (90 °C) mixtures of L-alanine or D-alanine with mercurous nitrate in distilled water precipitate elemental mercury and, by slow cooling and evaporation, give crystals that have been characterized as $[Hg_6(ala)_4(NO_3)_4]\cdot H_2O$

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Table 2. Ranges for interatomic distances (Å) in $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$

bond	L	D	typical ranges (ref)
$Hg^{I}-Hg^{I}$	2.5033(9)−2.5233(9); 3.0552(9)[a]	2.5045(5)−2.5233(5); 3.0558(6)[a]	2.50–2.52 (44−47)
$Hg^{I}-O$ (alanine)	2.122(9)−2.225(11)	2.145(6)−2.216(6)	2.09–2.15 (44−47)
$Hg^{I}-O$ (nitrate)	2.430(10)−3.060(14)	2.433(7)−3.030(9)	2.46–2.96 (57)
$Hg^{II}-N$	2.085(12)−2.125(12)	2.093(8)−2.115(8)	2.07–2.29 (4, 5, 16, 55, 56)
$Hg^{II}-O$ (alanine)	2.760(11)−2.865(9)	2.765(7)−2.862(6)	2.62–2.72 (4, 5, 16)
$Hg^{II}-O$ (nitrate)	2.645(10)−2.921(12)	2.653(6)−2.909(8)	2.59–2.77 (58)

[a] Closest contact between independent Hg_2^{2+} units.

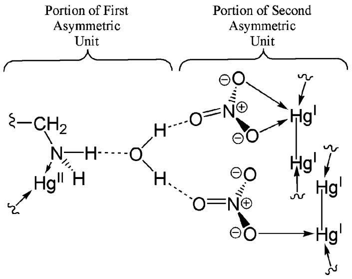
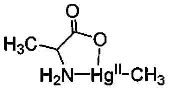


Figure 4. Hydrogen-bonding of one water molecule between two asymmetric units.

(empirical formula). It has not been possible to isolate complexes using similar procedures for mixtures of mercurous nitrate with the other 20 common amino acids. However, precipitation of elemental mercury is observed in reactions with nine amino acids (alanine, arginine, asparagine, glutamic acid, glutamine, glycine, proline, serine, and threonine).

The formula of the feature compound contains both mercury(I) centers and mercury(II) centers resulting from a disproportionation of mercurous ions to mercury(0) and mercury(II), consistent with the established effect of Lewis bases on mercury(I).[31,41] In the solid state, the asymmetric unit is composed of $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$, in which each alanine can be considered as an anion. The asymmetric unit associates into a polymeric chain of alternating mercury(I) pair−alanine and mercury(II)−alanine units, so that the monomeric unit consists of $[Hg^{I}_2Hg^{II}(ala)_2(NO_3)_2]$, as shown in Figure 3b. Pairs of mercury(I) centers interact with the oxygen atoms in the carboxylate groups and in four nitrate counterions. The eight mercury(I) atoms have coordination numbers of three (1), four (3), five (3), and six (1) (the number of mercury atoms with a specific coordination number is in parentheses). All four mercury(II) centers are eight-coordinate, involving interactions with the amino and carboxylate moieties in two alanine ligands and the oxygen atoms in two nitrate counterions. Within the inner coordination sphere, nitrogen atoms of the alanine ligands adopt a trans configuration about the mercury(II) centers (N−Hg−N, 168.4−175.1°). Carboxylate oxygen atoms are in a cis configuration about the mercury(II) centers with O−Hg−O angles between 62.6° and 71.0°. The mercury(II) atoms are chelated in a κ^2 fashion by each of two alanine molecules through Hg−N and Hg−O interactions, with typical Hg−N distances and slightly longer than expected Hg−O distances (Table 2); the N−Hg−O bond angle for each alanine ligand ranges between 62.4° and 66.2°.

The previously reported structure of methylmercury−alanine[4,5] contains a mercury(II) center chelated by one alanine ligand (**i**) with an almost linear N−Hg−C bond angle (173(1)°), a N−Hg bond distance of 2.10(3) Å, and a N−Hg−O bond angle of 58.6(7)°. In contrast, the mercury(II) center in $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$ accommodates two chelating alanine ligands (**ii**).



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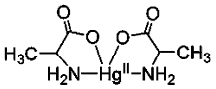

ii

Mercury(I) dimers are coordinated by oxygen atoms from alanine carboxylate groups and nitrate counterions. Hg−Hg−O (carboxylate) bond angles range from 158.4° to 174.1°. This near-linearity of the Hg−Hg−O moiety is present in the few other reported mercury(I)−carboxylate structures (166.6−177.9°; Table 2).[42–47] A close contact (3.0552(9) Å) between two mercury(I) atoms is responsible for the association of adjacent mercury(I) dimers (between Hg1 and Hg5 in Figure 3, cf. sum of the covalent radii,[48] 2.54 Å; sum of the van der Waals radii,[49] 4.1 Å). Mercury is known to form both neutral and ionic clusters with Hg−Hg bond distances varying between 2.66 and 3.85 Å,[50–54] and within the feature compound, eight Hg···Hg interdimer distances fall within this range.

The coordination spheres of the mercury atoms are completed by the nitrate counterions, in which the Hg−O

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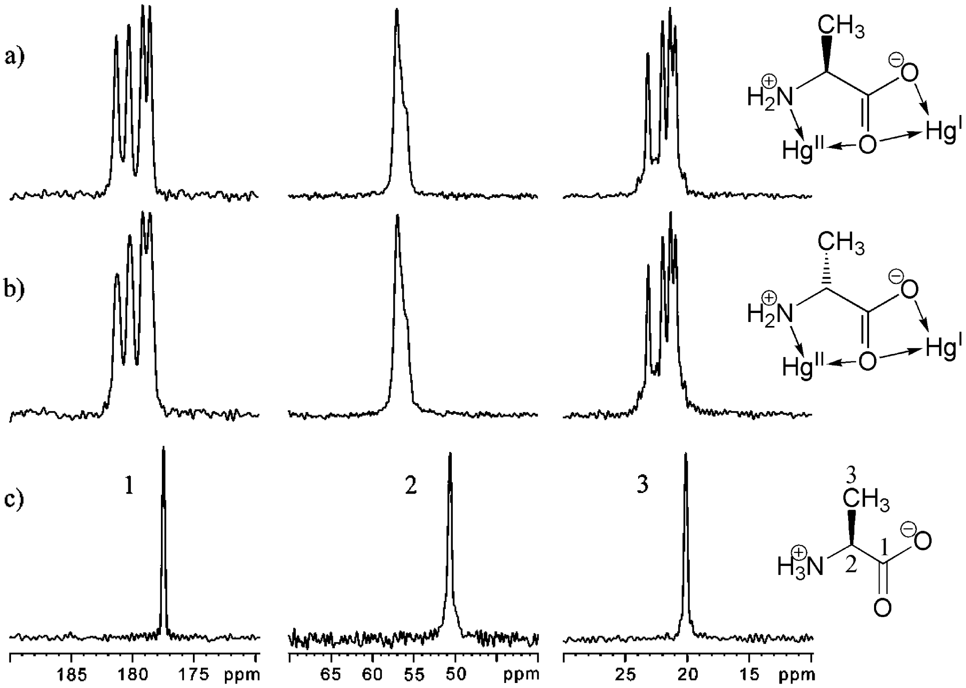

Figure 5. Solid-state ^{13}C CP-MAS NMR signals for (a) $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$, (b) $[Hg_{12}(D\text{-ala})_8(NO_3)_8]\cdot 2H_2O$, and (c) uncomplexed L-alanine.

Table 3. Solid-State ^{13}C NMR Chemical Shifts (ppm) for Solutions of $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ and L-Alanine

$[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$	L-alanine	assignment
181.3	177.5	**C**(O)
180.3		
179.2		
178.6		
57.0 (broad)	50.6	**C**(N)
23.2	20.1	**C**H$_3$
22.0		
21.5		
21.0		

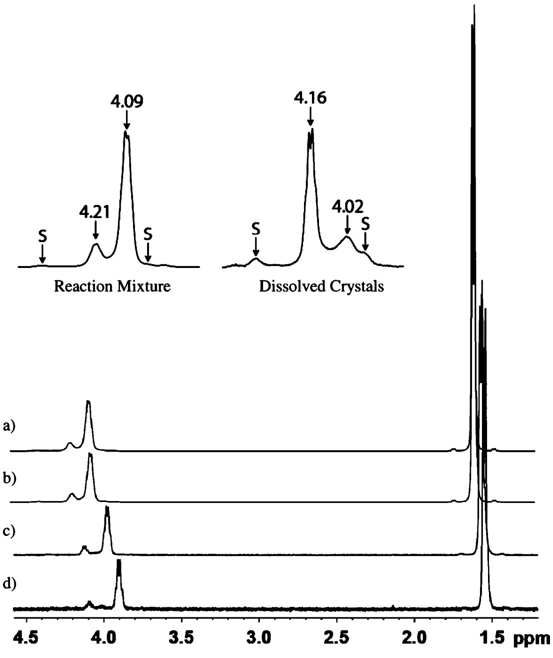

Figure 6. Solution-state ^1H NMR spectra of the reaction mixture of $[Hg_{12}(D\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ at (a) 0.125 M, (b) 0.080 M, (c) 0.010 M, and (d) 0.003 M. Inset: Comparison of methine signal for the reaction mixture (0.0125 M) and dissolved crystals (<0.0026 M); methine peaks (ppm) and potential mercury satellites (S) are labelled.

bond lengths are within the typical ranges (Table 2).[4,5,16,55,56] Each of two water molecules present in the asymmetric unit is hydrogen-bonded with the amine moiety of one alanine molecule (1.82–1.87 Å) and with the oxygen atoms of two nitrate counterions from the neighboring asymmetric unit (1.81–2.52 Å), Figure 4.

Solid-state ^{13}C CP-MAS NMR spectra for a crystalline sample of $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ is shown in Figure 5 and detailed in Table 3. In all cases, the spectroscopic data are reproducible for crystalline samples and are consistent for both isomers. The presence of water molecules perturbs the 2-fold (C_2) symmetry in the asymmetric unit of of $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$, (shown in Figure 3), which results in four different pairs of equivalent alanine ligands corresponding to four signals observed in the solid-state ^{13}C NMR spectra (Figure 5a and b). Poor resolution of the signals corresponding to the amine carbon center (C2) is due to ^{14}N quadrupolar broadening; however, the assymmetry of the peak indicates distinct broadened resonances.

The IR and Raman spectra for crystals of $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ or $[Hg_{12}(D\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ are consistent with those reported for the methylmercury–alanine complex.[5] Mercury–nitrogen IR stretching modes were assigned to the peaks at 525 and 553 cm^{-1} (**L**) or 526 and 557 cm^{-1} (**D**). The strong Raman mercury–mercury stretch of 160 cm^{-1} (**L**) or 159 cm^{-1} (**D**) was consistent with those previously reported for solvated mercury(I) ions (160–172 cm^{-1}).[31]

^1H NMR data for solutions of crystals of $[Hg_{12}(L\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ or $[Hg_{12}(D\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ dissolved in deuterium oxide and for the reaction mixtures (four concentrations) that give $[Hg_{12}(D\text{-ala})_8(NO_3)_8]\cdot 2H_2O$ are

Table 4. ESI-MS Data for the Reaction Mixtures of Mercurous Nitrate Dihydrate and Alanine (L, D, and a Racemic Mixture) with Distilled Water and 50% Methanol As Flow Solvents

	relative abundance[a]			
m/z	Hg + L-ala	Hg + D-ala	Hg + DL-ala	assignment $[Hg^{I}:Hg^{II}:ala]$
308	H (*L*)	H (*H*)	H (*L*)	$[0:1:1\text{–}1H+H_2O]^+$
863	M (*M*)	M (*H*)	M (*H*)	$[2:0:5\text{–}1H+H_2O]^+$
1151	L (*L*)	L (*L*)	L (*L*)	$[2:1:6\text{–}3H+H_2O]^+$

[a] H = 75–100%, M = 35–75%, and L = 3–35%; relative abundance values replicated within the given range for each flow solvent: distilled water (*50% Methanol*).

presented in Figures 1 and 6, respectively. In both cases, two distinct methine proton environments are observed (Figure 6, inset) that are tentatively rationalized in terms of the distinction between NO and OO κ^2 chelation of the mercury(II) and mercury(I) centers, respectively (Figure 5). ^{1}H NMR analysis of the reaction mixture also shows two environments for the alanine molecules. The chemical shifts are concentration-dependent and are more shielded at lower concentrations, while the shapes of the methine peaks do not change, as shown in Figure 6.

ESI-MS data obtained for reaction mixtures of mercurous nitrate with L-alanine, D-alanine, or DL-alanine (Table 4 and Figure 2a) and for solutions of crystals of $[Hg_{12}(L\text{-}ala)_8(NO_3)_8]\cdot 2H_2O$ or $[Hg_{12}(D\text{-}ala)_8(NO_3)_8]\cdot 2H_2O$ dissolved in distilled water or 50% methanol/water (v/v) show peaks at *m/z* 308, 863, and 1151. The peaks correspond to complex cations containing mercury and are observed independent of the flow solvent (distilled water and 50% methanol/water (v/v)). The assignments of *m/z* 308 as $[Hg^{II}(ala)\cdot H_2O-H]^+$, *m/z*863as$[Hg^{I}_2(ala)_5\cdot H_2O-H]^+$,and*m/z*1151as$[Hg^{I}_2Hg^{II}(ala)_6\cdot H_2O-3H]^+$ have been confirmed by comparison of experimental and calculated isotope peak patterns (Supporting Information), as well as tandem mass spectra for *m/z* 308 (Figure 2b). Alanine can hold a positive, neutral, or negative charge depending on the number of protons it possesses. The complex cation formulae observed in the ESI-MS are considered to contain neutral alanine ligands with a loss of protons ($-x$H) from the complex. Peaks corresponding to complexes with either and both mercury oxidation states are present in the ESI-mass spectrum, indicating that at least two alanine environments exist in the gas phase, consistent with observations from the solution ^{1}H NMR data.

Conclusion

An enantiomeric pair of new mercury−alanine complexes has been isolated from mixtures of mercurous nitrate and L- or D-alanine and comprehensively characterized as $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$. Both mercury(I) and mercury(II) are present in the structure. Mercury(II) results from a disproportionation process, consistent with the deposition of mercury(0), which is generally observed in reactions of mercurous with amino acids, and indicating that Hg(I) is a ready source of Hg(0) and Hg(II) in a biological environment. Crystallographic, spectroscopic, and spectrometric data for $[Hg_{12}(ala)_8(NO_3)_8]\cdot 2H_2O$ are interpreted in terms of two environments for alanine assigned as κ^2-OO coordination to mercury(I) and κ^2-NO coordination to mercury(II). The data represent a comprehensive characterization of the first example of a mercury−amino acid complex involving mercury(I).

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Supporting Information Available: X-ray crystallography, NMR spectroscopy, vibrational spectroscopy, and electrospray ionization mass spectrometry data. This material is available free of chrage via the internet at http://pubs.acs.org.

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