Hexanuclear hydrolysis products of the uracil nucleobase complex (1,3-dimethyluracil-5-yl)mercury(ii) nitrate

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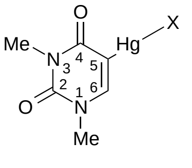
(1,3-Dimethyluracil-5-yl)mercury(II) nitrate undergoes, in aqueous solution, hydrolysis to the tris(1,3-dimethyluracil-5-yl)mercurioxonium salt, which dimerizes in two different ways *via* weak Hg···Hg contacts.

The propensity of mercury(ii) salts to undergo hydrolysis with formation of oligo- and poly-meric $[Hg(OH)]_n^{n+}$ or $[HgO]_n$ species is well established.[1] This feature is maintained in complexes of Hg^{II} containing one firmly bound ligand such as a methyl group. Thus, $[MeHg(H_2O)]^+$ forms, among others, the trismethylmercurioxonium cation, $[(MeHg)_3O]^+$,[2] which represents a very flat trigonal pyramid with the oxygen in the apical position.[3] $[(ClHg)_3O]^+$ has a very similar structure.[4] Here we report on hydrolysis products of an analogous complex with a C-bound uracil nucleobase (1,3-dimethyluracil, dmura) which have dimerized *via* one and two Hg···Hg contacts, respectively, of the Hg_3O to give hexanuclear compounds. This feature is reminiscent of the behaviour of phosphinegold(i) oxonium compounds, $[(R_3PAu)_3O]^+$.[5] This appears to be a consequence of the well known tendency of Au^I compounds to form weak Au–Au bonds and has been termed aurophilicity.[6]

We have recently described several examples of dmura nucleobase complexes containing Hg^{II} bound *via* the C-5 position.[7–9] Mercuriation of this site, although not fully unexpected,[10] was unusual considering previous findings.[11,12]

In the course of an NMR study on ligand exchange reactions of X[8] we observed precipitation of a colourless, crystalline compound from aqueous solution, pH 4 in the presence of $X = NO_3^-$.† X-Ray crystallography‡ revealed that the unit cell of the compound contains two different $[L_3Hg_3O]^+$ cations, **I** and **II** (L = 1,3-dimethyluracil-5-yl), each of which has a centrosymmetrically related counterpart (primed atoms), with which it is connected through weak Hg···Hg contacts. Cation **I** represents a very flat pyramid, whereas cation **II** is virtually planar (Fig. 1). Hg···Hg distances within the triangle of **I** range from 3.4705(5) to 3.5859(5) Å. The short contacts of 3.5620(5) Å between neighbouring cations involve Hg(1) and Hg(2′) as well as Hg(2) and Hg(1′) and generate a chairlike arrangement of the six mercury ions. In cation **II** the Hg···Hg separations range from 3.4552(6) to 3.5974(5) Å within the triangle. The closest intercationic Hg···Hg distance, between Hg(6) and Hg(6′) is only slightly longer, 3.6728(8) Å. All these Hg···Hg separations are significantly longer than those found in dinuclear mercury(i) complexes or in mercury clusters with Hg in the oxidation state zero,[13] but are close to or shorter than the sum of two van der Waals radii (1.7–2.0 Å).[14] Hg–O–Hg angles are within the range 116.0(3)–122.5(3)° and compare with those found in $[(MeHg)_3O]^+$ (116°)[3] and $[(ClHg)_3O]^+$ (118.9°).[4] The Hg–O distances are normal (av. 2.05 Å), as are the Hg–C distances to the nucleobases (2.05 Å[7–9]). Views perpendicular to the Hg_3 triangles and their centrosymmetrical counterparts (Fig. 2) clearly show that nucleobase stacking is not taking place, thereby excluding this possibility as a driving force for association of trinuclear entities.



Solid-state Raman spectra of Hdmura, $[Hg(dmura\text{-}C^5)(O_2CMe)]$ and $[Hg_6(dmura)_2O_2][NO_3]_2$ were compared.§

The ^1H NMR spectrum of the title compound in D_2O, pH* 4.9 [δ H-6, 7.40, $^3J(^1H–^{199}Hg)$ 189 Hz; δ CH_3, 3.40 and 3.30] is consistent with an oxygen donor *trans* to C-5 of dmura,[8] but permits no conclusions concerning the nature of the species in solution (monomer, trimer, hexamer).

However, ESI mass spectra¶ of D_2O and Me_2SO solutions of the title compound establish the formulation as [Hg6-

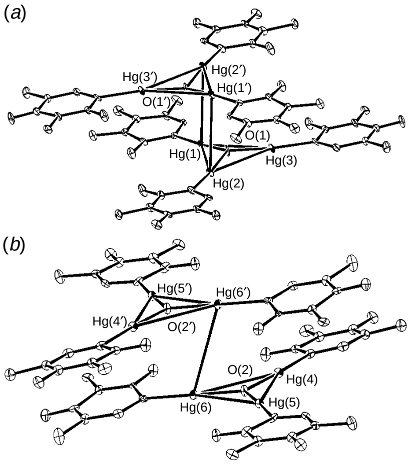


Fig. 1 Perspective view of centrosymmetrically related cations **I** (*a*) and **II** (*b*) of $[L_3Hg_3O][NO_3]\cdot 2H_2O$ (L = 1,3-dimethyluracil-5-yl). Ellipsoids are at the 30% probability level.

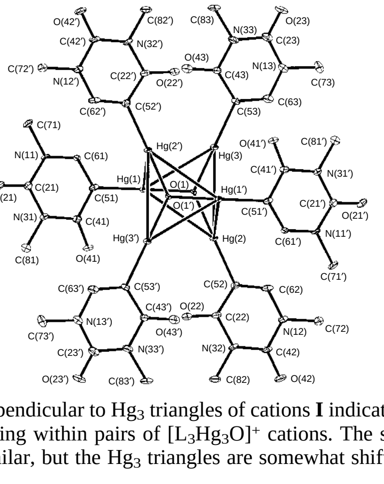


Fig. 2 View perpendicular to Hg_3 triangles of cations **I** indicating that there is no base stacking within pairs of $[L_3Hg_3O]^+$ cations. The situation with cations **II** is similar, but the Hg_3 triangles are somewhat shifted.

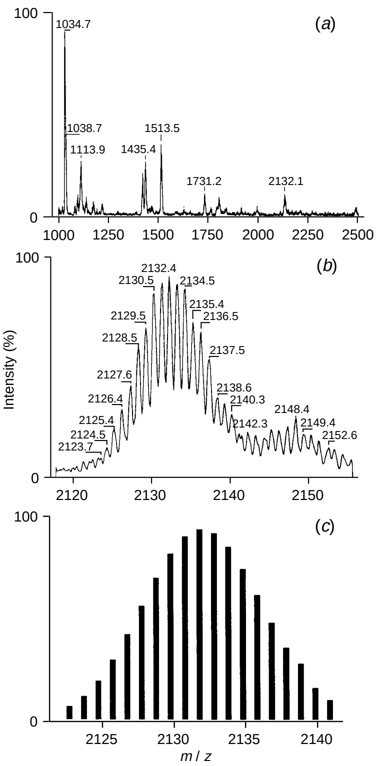


Fig. 3 Section of ESI mass spectrum of the title compound (*a*), of the [L$_6$Hg$_6$O$_2$(NO$_3$)]$^+$ peak (*b*) and calculated mass distribution for the latter peak (*c*)

(dmura)$_6$O$_2$][NO$_3$]$_2$ even under the conditions of the experiment: from the mass spectrum recorded of a Me$_2$SO solution (Fig. 3) the existence of [Hg$_6$(dmura)$_6$O$_2$(NO$_3$)]$^+$ is evident (*m*/*z* 2132.4), with excellent agreement between observed and calculated isotopic mass distributions. Signals due to [Hg$_3$(dmura)$_3$O]$^+$ (*m*/*z* 1034.7) are likewise observed, but the most intense signal centred at *m*/*z* 418.9 corresponds to [Hg(dmura)(Me$_2$SO)]$^+$. In aqueous solution the parent ion of the hexanuclear species is not observed, but fragments of the latter {[Hg$_4$(dmura)$_5$O]$^+$, *m*/*z* 1513.7; [Hg$_5$(dmura)$_5$O$_2$]$^+$, *m*/*z* 1729.5} point to its existence. The trinuclear species gives rise to an intense signal set at *m*/*z* 1035.5.

In conclusion, the solid-state structure of the title compound lends support to the option that [Hg$_3$(dmura)$_3$O]$^+$ cations, like [(R$_3$PAu)$_3$O]$^+$ cations, undergo association *via* Hg···Hg contacts. These appear to be sufficiently strong to survive ESIMS experiments.

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Footnotes

† In a typical experiment [Hg(dmura)(O$_2$CMe)] (0.1 mmol) in water (2 ml) was treated with either KNO$_3$ or AgNO$_3$ (0.3 mmol each). From the solution (pH 4), upon standing at room temperature, colourless crystals formed overnight in *ca.* 40% yield. Alternatively, reaction of Hg(NO$_3$)$_2$ and dmura (1:1, 60 °C, 24 h) in H$_2$O gave crystals of the title compound in 33% yield. {[Hg(dmura-*C*^{5})]$_3$O}NO$_3$·2H$_2$O, C$_{18}$H$_{25}$Hg$_3$N$_7$O$_{12}$ [Found (Calc.)]: C, 18.9 (19.1); H, 2.2 (2.2); N, 8.6 (8.6) %. IR (KBr) 1341 ν(NO$_3^-$), 1617 ν(C=C), 1670 cm^{-1} ν(C=O). ^{1}H NMR spectrum [200 MHz, (CD$_3$)$_2$SO, SiMe$_4$]: δ H-6, 7.35, δ CH$_3$, 3.32 and 3.19; ^3J(^{1}H–^{199}Hg) 190 Hz. ^{199}Hg NMR [35.79 MHz, (CD$_3$)$_2$SO, relative to HgMe$_2$] δ −1320.

‡ *Crystal data* for C$_{36}$H$_{50}$Hg$_6$N$_{14}$O$_{24}$: M = 2266.41, triclinic, space group $P\bar{1}$ (no. 2), a = 10.0050(2), b = 13.7841(2), c = 19.6534(2) Å, α = 99.797(1), β = 95.673(1), γ = 96.313(1) °, U = 2635.48(7) Å^3, Z = 2, D_c = 2.86 g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 175.9 cm^{-1}, F(000) = 2072, T = 153 K. The structure was solved by direct methods employing the SIR88 program[17] of the teXsan 1.7 software package[18] and refined by using the SHELXTL/PC software package[19] to R = 0.061 (R_w = 0.122) for 14 874 absorption-corrected (empirical corrections; transmission factors 0.23–0.80) reflections with $I > 2\sigma(I)$. A total of 38 024 (26 669 unique, R_{int} = 0.052) reflections were collected in the range $4 \leqslant 2\theta \leqslant 80°$ on a Siemens SMART area detector system using graphite-monochromated Mo-Kα radiation. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/353.

§ Bands at 215 and 109 cm^{-1} are tentatively assigned to ν[Hg–C(dmura)] and ν(Hg–O). The respective modes for [(MeHg)$_3$O]$^+$ in H$_2$O are at 570 and 134 cm^{-1}.[15] A band at 198 m cm^{-1} in the spectrum of [Hg(dmura-C^5)(O$_2$CMe)], absent in the spectrum of Hdmura, is assigned to ν[Hg–C(dmura)] from comparison with ν(Hg–Ph) modes.[16] Raman solution spectra could not be obtained due to insufficient solubility.

¶ Electrospray mass spectrometry (ESIMS) was performed on a Finnigan MAT 90 mass spectrometer equipped with an ESI II interface (Finnigan MAT, Bremen, Germany) operating in the positive mode. The mass spectra were acquired from *m*/*z* 250 to 2500 using scan rates between 5 and 100 s decade^{-1} and a resolution between 1000 and 2500. Water and Me$_2$SO solutions of the title compound were introduced into the ESI source at a flow rate of 0.5 μl min^{-1}. The temperature of the desolvation capillary was set to 200 °C.

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