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Tetrakis[μ-1,3-bis(4-methyl-2-pyridylimino)isoindolinato]trimercury(II) dinitrate methanol tetrasolvate

Mark Wicholas,[a]* Brandon L. Dietrich,[a] Oren P. Anderson[b] and Agnete la Cour[b]

[a]Department of Chemistry, Western Washington University, Bellingham, Washington 98225, USA, and [b]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

Correspondence e-mail:
wicholas@chem.wwu.edu

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The title compound, $[Hg_3(C_{20}H_{16}N_5)_4](NO_3)_2{\cdot}4CH_3OH$, consists of a trinuclear Hg^{II} dipositive cation, $[Hg_3(4'\text{-Me}L)_4]^{2+}$, two nitrate anions and four occluded methanol molecules. The Hg atoms of the cation lie on a crystallographic twofold axis and are tetrahedrally coordinated by nitrogen-donor atoms of the bridging 1,3-bis(4-methyl-2-pyridylimino)-isoindoline ligands. The central Hg atom is coordinated by four pyridine N atoms, one from each of the $4'\text{-Me}L^-$ ligands, while the two outer Hg atoms are each coordinated by two pyridine and two pyrrole N atoms.

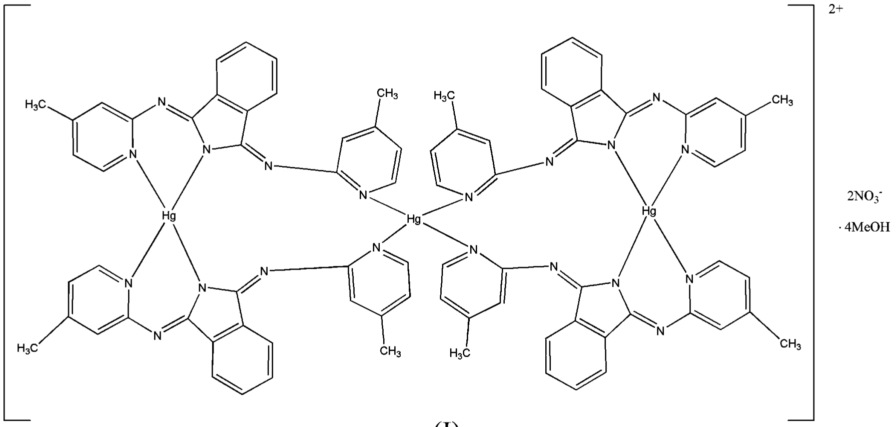
Key indicators

Single-crystal X-ray study
T = 165 K
Mean σ(C–C) = 0.007 Å
H-atom completeness 81%
R factor = 0.033
wR factor = 0.066
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Tridentate nitrogen-donor ligands have played an important role in inorganic chemistry in recent years as templates for models of metalloproteins and as templates for catalytic processes (Chaudhuri & Wieghardt, 1987; Trofimenko, 1999). The pyridine-arm isoindoline 4′-Me*L*H [1,3-bis(4-methyl-2-pyridylimino)isoindoline] when deprotonated normally coordinates meridionally to metal ions *via* a pyrrole and two pyridine N atoms and forms a series of bis-tridentate octahedral complexes $M(4'\text{-Me}L)_2$ with the divalent first row transition metal ions, M = Mn–Zn (Gagné *et al.*, 1981). We have shown through serendipitous discovery that 4′-Me*L*H when deprotonated reacts with zinc perchlorate in an equimolar ratio to form the trinuclear complex $[Zn_3(C_{20}H_{16}N_5)_4](ClO_4)_2{\cdot}5H_2O$, which contains tetrahedrally coordinated Zn atoms (Anderson *et al.*, 2003). In an effort to determine whether other d^{10} metal ions form similar tetrahedrally coordinated trinuclear complexes, we have examined the reactions of 4′-Me*L*H with Cd^{II} and Hg^{II}.



(I)

While we have been unsuccessful in preparing the Cd^{II} trinuclear congener, perhaps because of the known preference of Cd^{II} for octahedral coordination (Sigel & Martin, 1994), the title trinuclear Hg^{II} complex, (I), is formed readily from the reaction of mercuric nitrate and deprotonated 4′-Me*L*H.

The cation in the title compound is composed of two short helices of opposite hand, one coiling around Hg1 and one coiling around Hg3, that meet at Hg2. The three Hg atoms are located on a crystallographic twofold axis, and thus form a linear backbone for the complex cation. As a result, the trinuclear cation has crystallographic twofold symmetry about that Hg_3 axis. The crystallographically unique nitrate anion exhibits no sign of disorder, presumably because of multiple weak [O⋯O = 2.966 (8)–3.137 (7) Å] hydrogen bonding between its O atoms and the hydroxyl groups of the occluded methanol molecules.

Experimental

The isoindoline ligand was prepared by a solid state melt reaction (Addison & Burke, 1981). Solid $Hg(NO_3)_2\cdot 3H_2O$ (346 mg, 0.914 mmol) was added to 25 ml of a warm methanol solution (25 ml) of 4′-Me*L*H (327 mg, 1.0 mmol), which had been deprotonated by the addition of 1.0 *M* Bu_4NOH (1.0 ml, 1.0 mmol) in methanol. The orange–yellow solution was refluxed vigorously for 2 h, and the resulting orange solution was filtered while warm to remove cloudiness. Evaporation of the solvent from the filtrate over a two-day period produced large yellow crystals (45% yield) of (I), which were washed with ice-cold methanol and air-dried.

Crystal data

$[Hg_3(C_{20}H_{16}N_5)_4](NO_3)_2\cdot 4CH_4O$
$M_r = 2143.34$
Monoclinic, $C2/c$
$a = 26.285$ (5) Å
$b = 19.755$ (4) Å
$c = 19.376$ (4) Å
$\beta = 126.24$ (3)°
$V = 8115$ (3) $Å^3$

$Z = 4$
$D_x = 1.754$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 5.74$ mm^{-1}
$T = 165$ (2) K
Prism, yellow
0.55 × 0.50 × 0.33 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.145$, $T_{max} = 0.253$ (expected range = 0.086–0.151)

33142 measured reflections
8318 independent reflections
6461 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 26.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.066$
$S = 0.97$
8318 reflections
542 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 1.09$ e $Å^{-3}$
$\Delta\rho_{min} = -1.75$ e $Å^{-3}$

H atoms of the cation were placed in idealized positions and refined using a riding model with C—H = 0.93 and 0.96 Å, and with $U_{iso}(H) = 1.2U_{eq}$(aromatic C) and $1.5U_{eq}$(methyl C). H atoms were not included for the occluded methanol molecules, due to the fact that they could not be located in the difference map. While the highest peak in the difference map was 1.26 Å from C41, the next 19 peaks were due to residual density from the Hg atoms. The deepest hole in the map was 0.90 Å from Hg3.

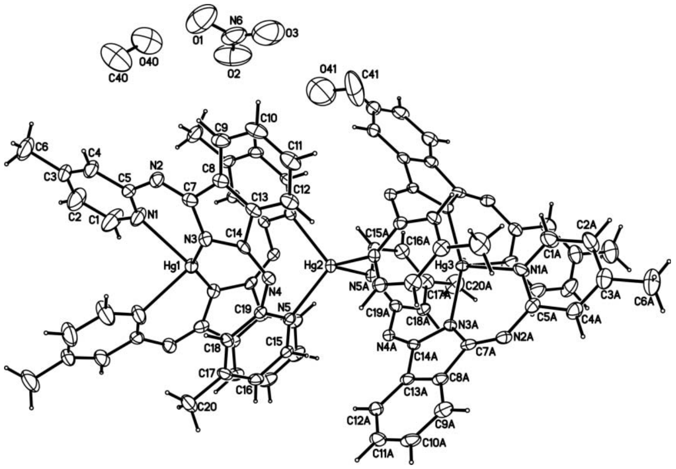


Figure 1
The structure of the trinuclear complex cation (50% probability displacement ellipsoids). Unlabeled atoms of the cation are related to the labeled atoms by operation of the twofold crystallographic symmetry axis through the three Hg atoms $(-x, y, \frac{1}{2} - z)$; a symmetry-related nitrate anion and two symmetry-related occluded methanol molecules are not shown.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003; data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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