

Tris(1,10-phenanthroline)nickel(II) di- μ -iodo-bis(diiodomercurate) *N,N*-dimethylformamide solvate monohydrateHua Fang^{a*} and Xuya Dai^b^aDepartment of Chemistry and Environment Engineering, Wuhan Polytechnic University, Wuhan, Hubei 430070, People's Republic of China, and ^bDepartment of Chemistry, Central China Normal University, Wuhan, Hubei 430079, People's Republic of ChinaCorrespondence e-mail:
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Key indicators

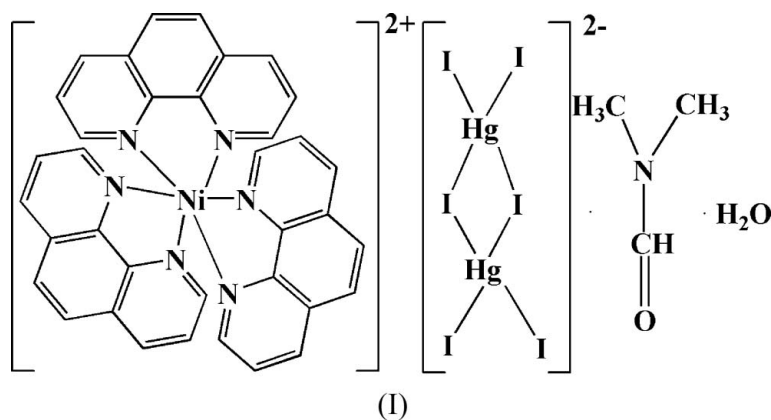
Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å
 R factor = 0.041
 wR factor = 0.095
Data-to-parameter ratio = 20.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3][\text{Hg}_2\text{I}_6] \cdot \text{C}_3\text{H}_7\text{NO} \cdot \text{H}_2\text{O}$, the Ni^{II} center has a distorted octahedral coordination geometry formed by six N atoms from three phen ligands. Each Hg^{II} ion is coordinated by two monodentate and two bidentate I^- ions in a distorted tetrahedral geometry.

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Comment

There is increasing interest in studying polyiodides because of their variety of applications (Füllbier, 1990; Svensson & Kloo, 1999). We report here the crystal structure of such an Hg^{II} compound, $[\text{Ni}(\text{phen})_3][\text{Hg}_2\text{I}_6] \cdot \text{DMF} \cdot \text{H}_2\text{O}$, (I), where phen is 1,10-phenanthroline and DMF is *N,N*-dimethylformamide.



The crystal structure contains discrete $[\text{Ni}(\text{phen})_3]^{2+}$ cations and $[\text{Hg}_2\text{I}_6]^{2-}$ anions (Fig. 1). The Ni^{II} center in the $[\text{Ni}(\text{phen})_3]^{2+}$ cation is six-coordinated by the six N atoms of three phen ligands, forming a distorted octahedral geometry. The Ni–N distances lie in the range 2.083 (4)–2.107 (5) Å, and the C–N and C–C distances in the phen ligands are normal (Table 1).

Each Hg^{II} atom of the $[\text{Hg}_2\text{I}_6]^{2-}$ anion is coordinated by four I^- ions in a distorted tetrahedral geometry. The bridging Hg–I bond distances range from 2.9101 (7) to 2.9525 (7) Å, and those in the terminal positions range from 2.6907 (6) to 2.7265 (6) Å. These values are in agreement with those reported for $[\text{Cu}(\text{phen})_3][\text{Hg}_2\text{I}_6] \cdot \text{DMSO} \cdot \text{H}_2\text{O}$ [2.9020 (8)–2.9499 (8) Å for bridging iodide and 2.6903 (8)–2.7301 (7) Å for terminal iodide; Oh *et al.*, 2006]. However, the Hg–I distances in (I) deviate slightly from those in the $[\text{Hg}_2\text{I}_6]^{2-}$ anion of $[\text{hmtH}]_2[\text{Hg}_2\text{I}_6]_{1/2}[\text{HgI}_3]_{1/2}\text{I}_2$ [2.8691 (9)–3.104 (5) Å for bridging iodide and 2.658 (2)–2.7183 (15) Å for terminal iodide; Svensson & Kloo, 1999], where hmt is hexamethylenetetramine.

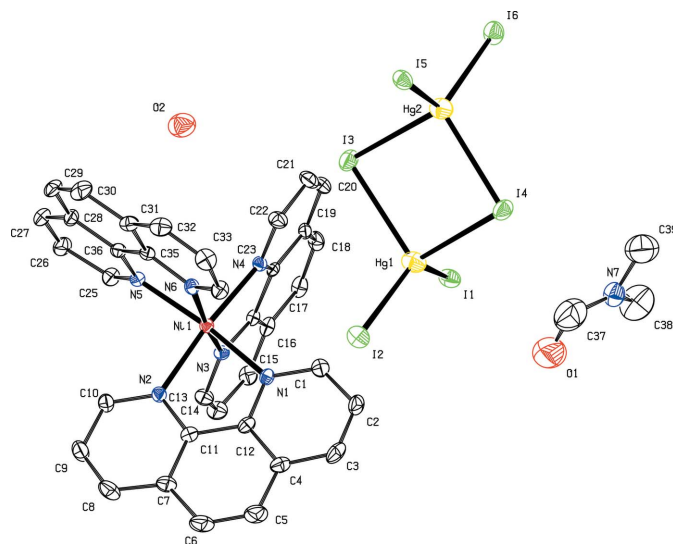


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. For the sake of clarity, H atoms have been omitted.

In the crystal structure, no hydrogen-bonding interactions are observed between $[\text{Ni}(\text{phen})_3]^{2+}$ cations and $[\text{Hg}_2\text{I}_6]^{2-}$ anions. There is an O—H...O hydrogen bond between the water and *N,N*-dimethylformamide molecules (Table 2).

Experimental

To a mixture of NaI (0.030 g, 0.2 mmol) and HgI_2 (0.454 g, 1 mmol) in acetone (20 ml), a solution of $[\text{Ni}(\text{phen})_3]\text{Cl}_2$ (0.351 g 0.5 mmol) in *N,N*-dimethylformamide (5 ml) was added with continuous stirring at 300 K. The mixture was stirred at room temperature for 2 h. After being filtered, the colourless solution was allowed to stand at room temperature. Two different types of crystals *viz.* colourless prism-shaped and red block-shaped crystals were obtained after slow evaporation of the solvent over a period of about two months. Red crystals of (I) were collected for X-ray crystallographic study.

Crystal data

$[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3][\text{Hg}_2\text{I}_6] \cdot \text{C}_3\text{H}_7\text{NO} \cdot \text{H}_2\text{O}$	$V = 4750.8$ (11) \AA^3
$M_r = 1853.01$	$Z = 4$
Monoclinic, $P2_1/c$	$D_x = 2.591$ Mg m^{-3}
$a = 12.6312$ (17) \AA	Mo $K\alpha$ radiation
$b = 18.756$ (3) \AA	$\mu = 10.78$ mm^{-1}
$c = 20.197$ (3) \AA	$T = 292$ (2) K
$\beta = 96.846$ (2)°	Block, red
	$0.32 \times 0.26 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	30627 measured reflections
φ and ω scans	10830 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	7281 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.130$, $T_{\max} = 0.247$	$R_{\text{int}} = 0.039$
(expected range = 0.076–0.144)	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.095$
 $S = 0.98$
 10830 reflections
 522 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.01 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.81 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , °).

Hg1–I2	2.6907 (6)	I3–Hg2	2.9168 (7)
Hg1–I1	2.6924 (6)	I4–Hg2	2.9101 (7)
Hg1–I4	2.9280 (7)	Hg2–I6	2.6892 (7)
Hg1–I3	2.9525 (7)	Hg2–I5	2.7265 (6)
I2–Hg1–I1	124.290 (19)	I6–Hg2–I5	118.915 (19)
I2–Hg1–I4	113.44 (2)	I6–Hg2–I4	113.02 (2)
I1–Hg1–I4	107.38 (2)	I5–Hg2–I4	107.93 (2)
I2–Hg1–I3	108.99 (2)	I6–Hg2–I3	114.31 (2)
I1–Hg1–I3	104.57 (2)	I5–Hg2–I3	105.198 (18)
I4–Hg1–I3	93.392 (17)	I4–Hg2–I3	94.515 (17)

Table 2

Hydrogen-bond geometry (\AA , °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O2–H2B...O1 ¹	0.83 (4)	1.93 (5)	2.706 (13)	158 (13)

Symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

All H atoms were initially located in a difference Fourier map. The water H atoms were refined with an O—H distance restraint of 0.82 (1) \AA , and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms with C—H = 0.93 or 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The U^{ij} components of atoms N7, C37, C38 and C39 were restrained to approximately isotropic behaviour.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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