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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(C-C)$ = 0.005 Å
R factor = 0.020
wR factor = 0.056
Data-to-parameter ratio = 17.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[1-hydroxy-4,4,5,5-tetramethyl-2-(1,3-thiazol-2-yl- κN)-2,3-dihydro-1*H*-imidazole- κN^3]dinitrato-mercury(II)

In the title complex, $[\text{Hg}(\text{NO}_3)_2(\text{C}_{10}\text{H}_{15}\text{N}_3\text{OS})_2]$, the Hg^{II} ion (site symmetry $\bar{1}$) adopts a grossly distorted octahedral geometry by chelation of two neutral Him-thz ligands [Him-thz is 2-(2'-thiazole)-4,4,5,5-tetramethyldihydro-1*H*-imidazolyl-1-hydroxy] through their thiazole N atoms [$\text{Hg}-\text{N} = 2.846(2)$ Å] and reduced imino nitroxide N atoms [$\text{Hg}-\text{N} = 2.055(2)$ Å], leading to a five-membered ring, together with two O atoms from two nitrate anions [$\text{Hg}-\text{O} = 2.859(3)$ Å]. The molecules form one-dimensional chains by way of intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

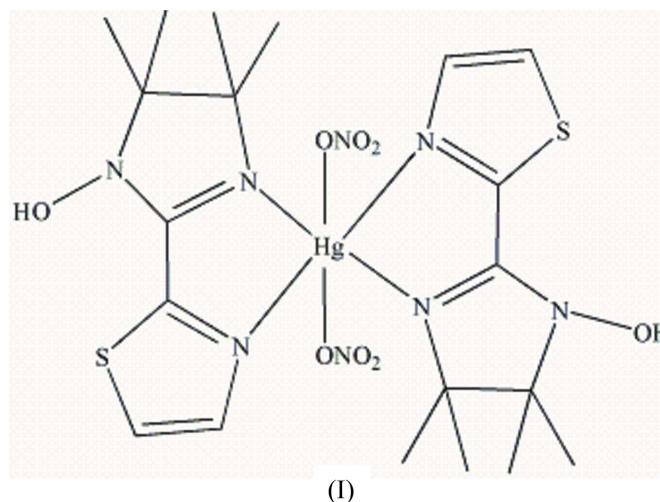
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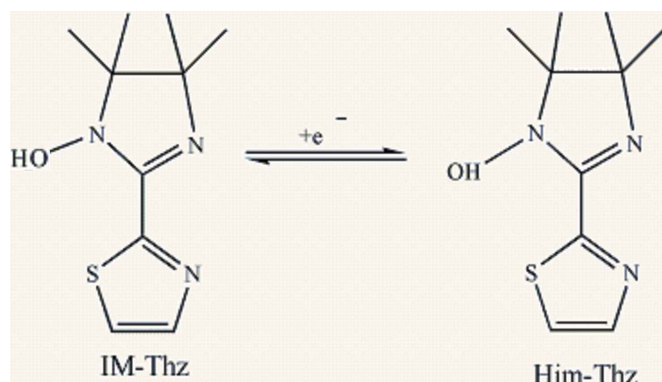
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Comment

The engineering of molecular magnets constitutes a major contemporary research aim and has spawned interest in organic radicals as building blocks for the construction of such materials (Yamamoto *et al.*, 2001; Aoki *et al.*, 2003; Iino *et al.*, 2003; Pillet *et al.*, 2001). In the past two decades, there have been a large number of investigations on the magneto/structural chemistry of transition metal complexes containing nitronyl and imino nitroxide radicals (Taylor *et al.*, 2003; Zhou *et al.*, 2004; Wang *et al.*, 2003; Ruiz *et al.*, 2000). However, nitroxide radicals can undergo redox reactions with transition metal ions and the mechanistic details of the reduction of the imino radicals are not completely clear. It is likely that the imino radicals are reduced by acidic impurities or other experimental conditions during the reaction process (Jiang *et al.*, 1998; Li *et al.*, 2001). In this paper, we report the synthesis and crystal structure of the title compound, (I) (Fig. 1), $\text{Hg}(\text{Him-thz})_2(\text{NO}_3)_2$, where Him-thz = 2-(2'-thiazole)-4,4,5,5-tetramethyldihydro-1*H*-imidazolyl-1-hydroxy), *i.e.* the reduced IM-thz radical.





The mercury(II) ion (site symmetry $\bar{1}$) in (I) is six-coordinated in a grossly distorted octahedral HgN_4O_2 environment. Two Him-thz molecules, acting as bidentate chelating ligands, coordinate the mercury(II) ion through a very long (Table 1) $\text{Hg}-\text{N}$ bond from the N atom of the thiazole ring and a short $\text{Hg}-\text{N}$ bond from the N atom of the imidazole ring, leading to a five-membered chelate rings. The mercury coordination is completed by long $\text{Hg}-\text{O}$ bonds to nearby monodentate nitrate anions. Similar $\text{Hg}-\text{N}$ and $\text{Hg}-\text{O}$ bond lengths have been seen in other complexes (Lee *et al.*, 1998; Kim *et al.*, 1998).

Molecules of (I) are linked into chains by way of an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond (Fig. 2 and Table 2) involving a reduced $\text{N}-\text{OH}$ group as donor and a nitrate O atom as acceptor.

Experimental

IM-thz was synthesized using a method in the literature (Ullman *et al.*, 1972). Diethyl ether vapor was diffused into an acetonitrile solution (6 ml) containing $\text{Hg}(\text{NO}_3)_2$ (0.25 mmol) and IM-thz (0.5 mmol) in a closed vessel in the dark for two weeks, affording red blocks of (I) suitable for X-ray analysis. Analysis calculated for $\text{C}_{20}\text{H}_{30}\text{HgS}_2\text{N}_8\text{O}_8$: C 30.98, H 3.90, N 14.46%; found: C 31.03, H 3.81, N 14.37%.

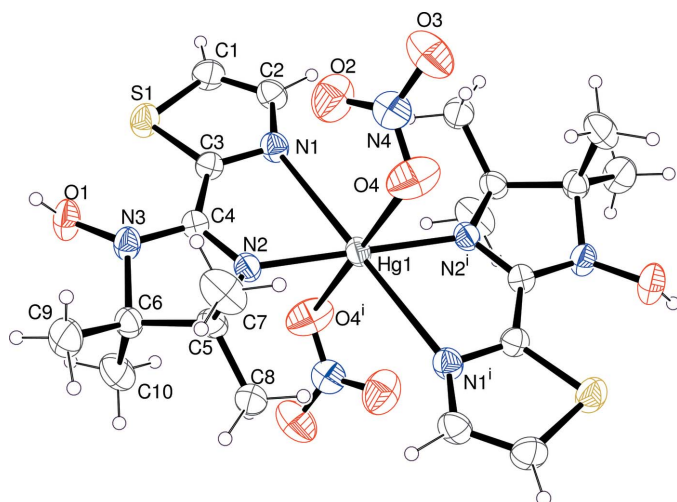


Figure 1
View of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

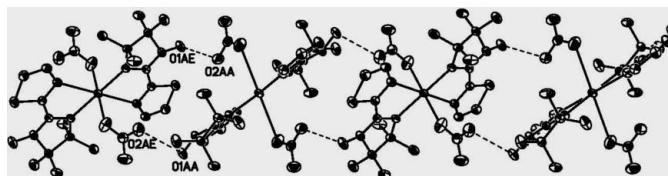


Figure 2
Detail of (I), showing the intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds as dashed lines.

Crystal data

$[\text{Hg}(\text{NO}_3)_2(\text{C}_{10}\text{H}_{15}\text{N}_3\text{OS})_2]$
 $M_r = 775.22$
 Monoclinic, $C2/c$
 $a = 19.758$ (4) Å
 $b = 13.580$ (3) Å
 $c = 11.587$ (3) Å
 $\beta = 115.739$ (3)°
 $V = 2800.3$ (11) Å³
 $Z = 4$

$D_x = 1.839$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6354 reflections
 $\theta = 2.3$ – 28.7°
 $\mu = 5.70$ mm⁻¹
 $T = 295$ (2) K
 Block, red
 $0.36 \times 0.24 \times 0.15$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.202, T_{\max} = 0.425$
 11946 measured reflections

3212 independent reflections
 2498 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\max} = 27.5^\circ$
 $h = -25 \rightarrow 25$
 $k = -17 \rightarrow 17$
 $l = -15 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.056$
 $S = 1.03$
 3212 reflections
 183 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 3.1412P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.96$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 1

Selected bond lengths (Å).

Hg1–N2	2.055 (2)	N3–O1	1.391 (3)
Hg1–N1	2.846 (2)	C4–N2	1.313 (4)
Hg1–O4	2.859 (3)	C4–N3	1.342 (4)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}^{\text{ii}}$	0.82	1.96	2.737 (5)	158

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

The H atoms were positioned geometrically and refined using the riding-model approximation, with $\text{C}-\text{H} = 0.93$ or 0.96 Å and $\text{O}-\text{H} = 0.82$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl carrier})$.

Data collection: APEX II (Bruker, 2004); cell refinement: APEX II; data reduction: SAINT (Bruker 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker 2004); software used to prepare material for publication: SHELXTL.

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References

- Aoki, C., Ishida, T. & Nogami, T. (2003). *Inorg. Chem.* **42**, 7616–7625.
- Bruker (2004). *APEX II, SAINT* (Version 6.22) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Iino, A., Suzuki, T. & Kaizaki, S. (2003). *J. Chem. Soc. Dalton Trans.* pp. 4604–4611.
- Jiang, Z. H., Sun, B. W., Liao, D. Z., Wang, G. L., Donnadiou, B. & Tuchagues, J. P. (1998). *Inorg. Chim. Acta*, **279**, 76–84.
- Kim, K. M., Song, S. C., Lee, S. S., Kang, H. C. & Sohn, Y. S. (1998). *Inorg. Chem.* **7**, 5764–5768.
- Lee, C. L., Huang, C. H., Wei, H. H., Liu, Y. H., Lee, G. H. & Wang, Y. (1998). *J. Chem. Soc. Dalton Trans.* pp. 171–176.
- Li, L. C., Liao, D. Z., Jiang, Z. H. & Yan, S. P. (2001). *J. Mol. Struct.* **569**, 179–183.
- Pillet, S., Souhassou, M., Pontillon, Y., Caneschi, A., Gatteschi, D. & Lecomte, C. (2001). *New J. Chem.* **25**, 131–143.
- Ruiz, M. D., Sporer, C., Wurst, K., Jaitner, P. & Veciana, J. (2000). *Angew. Chem. Int. Ed.* **39**, 3688–3691.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Taylor, P., Serwiński, P. R. & Lahti, P. M. (2003). *Chem. Commun.* pp. 1400–1401.
- Ullman, E. F., Osiecki, J. H., Boocock, D. G. B. & Darcy, R. (1972). *J. Am. Chem. Soc.* **94**, 7049–7056.
- Wang, L. Y., Zhang, C. X., Liao, D. Z., Jiang, Z. H. & Yan, S. P. (2003). *J. Mol. Struct.* **657**, 1–6.
- Yamamoto, Y., Yoshida, T., Suzuki, T. & Kaizaki, S. (2001). *Inorg. Chim. Acta*, **325**, 187–192.
- Zhou, H. B., Wang, S. P., Dong, W., Liu, Z. Q., Wang, Q. L., Liao, D. Z., Jiang, Z. H., Yan, S. P. & Cheng, P. (2004). *Inorg. Chem.* **43**, 4552–4554.