A sensitive hydrazine hydrate sensor based on mercaptomethylterminated trinuclear Ni(II) complex modified gold electrode

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The crystallographic data for Ni3 are summarized in Table S1. The selected

interatomic distances and interatomic angles for Ni3 are summarized in Table S2.

X-ray Crystallography

The X-ray crystallographic data were collected using a Bruker Apex 2000 diffractometer equipped Mo K α radiation (graphite monochromated) ($\lambda = 0.71073$ Å) with the $\omega/2\theta$ scan mode at 153 K. Lorentz-polarization and absorption corrections were applied. The structure was solved by direct methods using the SHELXS-97 program, and refined using weighted full-matrix least-squares on F^2 . The refinement and further calculations were performed using the SHELXL-97 program. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic ligands were generated geometrically, while the hydrogen atoms of water molecules were found in the Fourier difference map. All the hydrogen atoms were assigned the same isotropic temperature factors and included in the structure factor calculations.

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Formula	$[Ni_3(C_3H_6N_4S)_6(OH)_6].$
Fw	1059.15
cryst syst	monoclinic
space group	C2/c
a, Å	19.7049(17)
b, Å	14.1790(12)
с, Å	23.480(2)
a, deg	90
β, deg	105.644(5)
γ, deg	90
V, Å ³	6317.2(9)
Z	4
Т, К	296(2)
d_{calcd} , g/cm^3	1.615
λ	0.71073
abs coeff, cm ⁻¹	4.743
<i>R1</i>	0.1439
wR2	0.4159

Table S1. Crystallographic data and structure refinements for Ni3

Table S2. Selected interatomic distances and interatomic angles for Ni3

N(1)-Ni(2) 2.	.095(10)	Ni(1)-O(2) 2	2.108(10)
N(2)-Ni(1) 2.	.048(12)	Ni(1)-O(3) 2	2.113(10)
N(5)-Ni(2)	2.122(9)	Ni(1)-O(1) 2	2.114(10)
N(6)-Ni(1) 2	.057(11)	Ni(2)-N(1) 2	.095(10)
N(9)-Ni(1) 2	.039(10)	Ni(2)-N(10) 2	.113(10)
N(10)-Ni(2) 2	.113(10)	Ni(2)-N(5)	2.122(9)
N(9)-Ni(1)-N(2)	94.5(4)	N(1)-Ni(2)-N(1)	180.0(1)
N(9)-Ni(1)-N(6)	93.1(4)	N(1)-Ni(2)-N(10)	93.0(4)
N(2)-Ni(1)-N(6)	93.2(4)	N(1)-Ni(2)-N(10)	87.0(4)
N(9)-Ni(1)-O(2)	173.1(4)	N(1)-Ni(2)-N(10)	87.0(4)
N(2)-Ni(1)-O(2)	91.4(4)	N(1)-Ni(2)-N(10)	93.0(4)
N(6)-Ni(1)-O(2)	90.1(4)	N(10)-Ni(2)-N(10) 180.0(7)
N(9)-Ni(1)-O(3)	86.9(4)	N(1)-Ni(2)-N(5)	88.1(4)
N(2)-Ni(1)-O(3)	176.6(4)	N(1)-Ni(2)-N(5)	91.9(4)
N(6)-Ni(1)-O(3)	89.8(4)	N(10)-Ni(2)-N(5)	87.0(4)
O(2)-Ni(1)-O(3)	87.0(4)	N(10)-Ni(2)-N(5)	93.0(4)
N(9)-Ni(1)-O(1)	92.6(4)	N(1)-Ni(2)-N(5)	91.9(4)
N(2)-Ni(1)-O(1)	89.9(4)	N(1)-Ni(2)-N(5)	88.1(4)
N(6)-Ni(1)-O(1)	173.3(4)	N(10)-Ni(2)-N(5)	93.0(4)
O(2)-Ni(1)-O(1)	83.9(5)	N(10)-Ni(2)-N(5)	87.0(4)
O(3)-Ni(1)-O(1)	87.0(4)	N(5)-Ni(2)-N(5)	180.0(1)







Figure S1 ¹H NMR (400 MHz) of the Ni3 complex ¹H NMR(400 MHz, (CD₃)₂CO):δ 10.86 (s, 1H,OH), 4.92 (s, 2H, NH₂), 1.30 (s, 3H, SCH₃).



Figure S2 FTIR spectrum of the Ni3 complex.

The strong and board band ranging from \sim 3600 to 2700 cm⁻¹ could be ascribed to stretching vibration of O-H, while the peaks at 3440 and 3344 cm⁻¹ belong to stretching vibration of N-H. As depicted in figure S2, 1645 cm⁻¹ represent stretching vibration of N= N, and the 1383 cm⁻¹ is the typical bending vibration of methyl (- CH₃).



Fig. S3. SWVs of the Au/Ni3 electrode in 0.1 M Na₂SO₄ solution containing 0.20, 0.25, and 0.30 mM hydrazine hydrate.



Fig. S4. SWV responses of 50 μ M hydrazine hydrate at the Ni3/Au electrode for 20 times of consecutive detection.