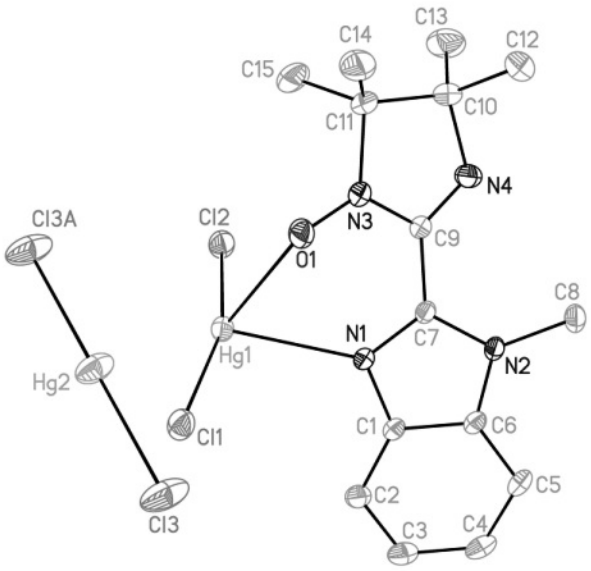
Synthesis and crystal structure of a new mercury(II) complex with imino nitroxide radical, $C_{30}H_{38}Cl_6Hg_3N_8O_2$

Chao-Jun He*, En-Pu Zu and Xiao-Jun Zhou

Luoyang Normal University, Life Science Department, Luoyang 471022, Henan Province, P. R. China

Received February 11, 2012, accepted July 19, 2012, available online October 05, 2012, CCDC no. 1267/3819



Abstract

$C_{30}H_{38}Cl_6Hg_3N_8O_2$, triclinic, $P\bar{1}$ (no. 2), a = 7.3649(5) Å, b = 11.4075(8) Å, c = 13.0120(9) Å, α = 100.454(1)°, β = 102.089(1)°, γ = 103.229(1)°, V = 1010.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.0202, $wR_{ref}(F^2)$ = 0.0502, T = 291 K.

Table 1. Data collection and handling.

Crystal:	deep red blocks, size 0.25×0.25×0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	118.09 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7751, 3705
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3424
$N(param)_{refined}$:	228
Programs:	SHELX [9]

Source of material

The imino nitroxide radical IM-1'-MeBzIm (IM-1'-MeBzIm = 2-{2'-[(1'-methyl)benzimidazolyl]}-4,4,5,5-tetramethyl-imidazoline-1-oxyl) was prepared by the literature method [1]. Complex $[HgCl_2(IM\text{-}1'\text{-}MeBzIm)]\cdot(HgCl_2)$ was synthesized as follows: to the solution of $HgCl_2$ (0.5mmol) in ethanol (15 mL) was added with stirring a solution of the IM-1`-MeBzIm (0.5 mmol) in ethanol (15 ml). The mixture was stirred further for two hours affording a color change from red to deep red, and then the reaction mixture was filtered. The clear deep red filtrate was diffused with diethyl ether vapour at room temperature. Deep red crystals were obtained in 45% yield.

* Correspondence author (e-mail: hchj98@163.com)

Discussion

The design and synthesis of molecule-based magnetic materials is one of the major subjects in material science. The families of radicals and the corresponding mental-radical complexes have attracted considerable attention and have been extensively studied in the quest for new molecule based magnetic materials for several years [2-4]. In many different types of organic radicals, research has focused on the nitronyl nitroxide radicals (NITR) family because of their flexibility and functionality. The nitronyl nitroxides substituted with phenyl, pyridyl, imidazolyl and benzimidazolyl groups have the advantage of forming stable chelated complexes with the support of auxiliary substituent-groups. Up to now, there have been a large number of investigations with regard to first-row transition metal complexes with NIT-R (R: pyridyl, imidazolyl, benzimidazolyl, thiazolyl, triazolyl, and so on) [5-8] concerning the corresponding structures and various properties especially the magnetic properties. In this article, we report the synthesis and crystal structures of a new mercury(II) complex involving benzimidazolyl -substituted iminol nitroxide radical.

A perspective view of the molecular structure of $[HgCl_2(IM\text{-}1'\text{-}MeBzIm)]\cdot(HgCl_2)$ is show in Figure 1. The compound consists of one discrete four-coordinated Hg(1) complex and one $HgCl_2$ molecule. The $[HgCl_2(IM\text{-}1'\text{-}MeBzIm)]$ moiety, consists of one mercury(II) ion, one chelating IM-1'-MeBzIm ligand and two chloride anions. The IM-1'-MeBzIm ligands are coordinated to the Hg atom with a κ_2-*N*(MeBzIm), O(IM) mode to avoid steric hindrance with the methyl group. The Hg(1) atom has a distorted-tetrahedral coordination by virtue of chelating O(1) and N(1) atoms of radical ligand and two terminal Cl(1) and Cl(2) atoms. The bond lengths Hg(1)–Cl(1), Hg(1)–Cl(2), Hg(1)–O(1) and Hg(1)–N(1) are 2.3223(11) Å, 2.3307(11) Å, 2.678(3) Å and 2.462(3) Å, respectively. The bond angle of Cl(1)–Hg(2)–Cl(2) is 162.51(4)°. Atom Hg(2), originally coordinated by two chloride anions, has a linear coordination [Cl(3)–Hg(2)–Cl(3#1) 176.61(8)°, Hg(2)–Cl(3) 2.3038(11) Å and Hg(2)–Cl(3#1) 2.3037(11) Å] (Symmetry code: #1 -x+2, -y, -z+2). The fragment O(1)–N(3)–C(9)–N(4) is nearly planar, but forms a dihedral angle of 31.236(224)° with the plane of the benzimidazole ring. The coordinated N(3)–O(1) bond length is 1.278(4) Å. There exist intermolecular interactions in the crystal via a weak Hg···Cl coordinated bond with Hg(1)···Cl(3) = 3.235 Å, Hg(1)···Cl(3#1) = 3.236 Å, Hg(2)···Cl(1) = 3.060 Å, Hg(2)···Cl(2) = 3.180 Å. There is five-coordination around Hg(1) and six-coordination around Hg(2), leading to a chain-like motif in the structure. Therefore, formation of one dimensional chains is constructed through weak Hg–Cl bonds.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	2*i*	0.1618	–0.1899	0.6533	0.061
H(3)	2*i*	–0.0121	–0.3335	0.4953	0.072
H(4)	2*i*	–0.0407	–0.2847	0.3311	0.075
H(5)	2*i*	0.1131	–0.0894	0.3163	0.062
H(8A)	2*i*	0.3538	0.1114	0.3525	0.078
H(8B)	2*i*	0.4741	0.2320	0.4418	0.078
H(8C)	2*i*	0.2494	0.2053	0.4000	0.078
H(12A)	2*i*	0.8240	0.4719	0.6241	0.115
H(12B)	2*i*	0.8383	0.6089	0.6796	0.115
H(12C)	2*i*	0.6821	0.5403	0.5702	0.115
H(13A)	2*i*	0.4282	0.5853	0.6516	0.146
H(13B)	2*i*	0.5768	0.6520	0.7639	0.146
H(13C)	2*i*	0.3970	0.5429	0.7562	0.146
H(14A)	2*i*	0.9686	0.4369	0.8893	0.128
H(14B)	2*i*	0.9691	0.5705	0.8751	0.128
H(14C)	2*i*	0.9743	0.4689	0.7777	0.128
H(15A)	2*i*	0.4859	0.4443	0.8790	0.153
H(15B)	2*i*	0.6638	0.5612	0.9312	0.153
H(15C)	2*i*	0.6728	0.4326	0.9554	0.153

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	2*i*	0.40705(2)	0.06853(1)	0.85696(1)	0.0601(1)	0.05040(9)	0.03959(9)	0.01912(7)	0.01509(7)	0.01277(6)
Cl(1)	2*i*	0.5785(2)	–0.0783(1)	0.86653(8)	0.0826(8)	0.0740(7)	0.0497(5)	0.0429(6)	0.0104(5)	0.0145(5)
Cl(2)	2*i*	0.2213(2)	0.2023(1)	0.89666(9)	0.0885(8)	0.0658(6)	0.0573(6)	0.0382(6)	0.0281(6)	0.0163(5)
Hg(2)	1*a*	1	0	1	0.0690(2)	0.0624(2)	0.0649(2)	0.0025(1)	0.0334(1)	–0.0113(1)
Cl(3)	2*i*	1.0470(2)	–0.1475(1)	0.8696(1)	0.0881(9)	0.0710(7)	0.098(1)	–0.0036(6)	0.0528(8)	–0.0260(7)
O(1)	2*i*	0.6930(4)	0.2321(3)	0.8178(2)	0.060(2)	0.062(2)	0.045(1)	0.008(1)	0.000(1)	0.017(1)
N(1)	2*i*	0.3497(4)	0.0548(2)	0.6613(2)	0.048(2)	0.038(1)	0.031(1)	0.012(1)	0.009(1)	0.006(1)
N(2)	2*i*	0.3270(4)	0.1019(3)	0.5004(2)	0.044(2)	0.044(1)	0.029(1)	0.016(1)	0.010(1)	0.009(1)
N(3)	2*i*	0.6369(5)	0.3059(3)	0.7634(2)	0.056(2)	0.046(2)	0.034(1)	0.008(1)	0.007(1)	0.007(1)
N(4)	2*i*	0.4720(5)	0.3652(3)	0.6266(3)	0.062(2)	0.041(2)	0.054(2)	0.009(1)	0.005(2)	0.010(1)
C(1)	2*i*	0.2408(5)	–0.0505(3)	0.5810(3)	0.042(2)	0.041(2)	0.035(2)	0.014(1)	0.011(1)	0.003(1)
C(2)	2*i*	0.1519(6)	–0.1688(3)	0.5870(3)	0.053(2)	0.043(2)	0.054(2)	0.010(2)	0.017(2)	0.007(2)
C(3)	2*i*	0.0490(6)	–0.2536(4)	0.4926(4)	0.057(2)	0.044(2)	0.071(3)	0.006(2)	0.020(2)	–0.001(2)
C(4)	2*i*	0.0327(6)	–0.2243(4)	0.3932(4)	0.057(2)	0.055(2)	0.056(2)	0.009(2)	0.008(2)	–0.016(2)
C(5)	2*i*	0.1219(6)	–0.1085(4)	0.3834(3)	0.052(2)	0.062(2)	0.034(2)	0.017(2)	0.007(2)	–0.003(2)
C(6)	2*i*	0.2270(5)	–0.0207(3)	0.4802(3)	0.042(2)	0.044(2)	0.034(2)	0.018(1)	0.008(1)	0.003(1)
C(7)	2*i*	0.3954(5)	0.1426(3)	0.6100(3)	0.043(2)	0.040(2)	0.029(2)	0.015(1)	0.008(1)	0.006(1)
C(8)	2*i*	0.3533(6)	0.1683(4)	0.4165(3)	0.062(2)	0.062(2)	0.039(2)	0.022(2)	0.016(2)	0.020(2)
C(9)	2*i*	0.5001(5)	0.2725(3)	0.6642(3)	0.051(2)	0.039(2)	0.034(2)	0.011(1)	0.011(1)	0.007(1)
C(10)	2*i*	0.6074(7)	0.4823(3)	0.7012(4)	0.073(2)	0.039(2)	0.060(2)	0.009(2)	0.015(2)	0.005(2)
C(11)	2*i*	0.7049(7)	0.4437(4)	0.8043(3)	0.074(2)	0.043(2)	0.047(2)	0.003(2)	0.014(2)	–0.001(2)
C(12)	2*i*	0.7515(8)	0.5304(4)	0.6378(4)	0.092(3)	0.062(3)	0.070(3)	0.003(2)	0.024(3)	0.021(2)
C(13)	2*i*	0.4919(9)	0.5739(5)	0.7199(5)	0.119(5)	0.062(3)	0.115(5)	0.040(3)	0.031(4)	0.010(3)
C(14)	2*i*	0.9245(7)	0.4837(5)	0.8399(4)	0.079(3)	0.070(3)	0.080(3)	–0.008(3)	–0.003(3)	0.013(3)
C(15)	2*i*	0.624(1)	0.4732(5)	0.9014(4)	0.161(5)	0.072(3)	0.066(3)	0.015(4)	0.057(3)	–0.010(3)

References

1. Ullman, E. F.; Osiechi. J. H.: Stable free radicals. X. Nitronyl nitroxide monoradicals and biradicals as possible small molecule spin labels. J. Am. Chem. Soc. **94** (1972) 7049-7059.
2. Kahn, O. Molecular Magnetism; VCH: New York, 1993.
3. Vostrikova, K. E.; Luneau, D.; Wernsdorfer, W. Rey, P.; Verdaguer, M.: A S = 7 Ground Spin-State Cluster Built from Three Shells of Different Spin Carriers Ferromagnetically Coupled, Transition-Metal Ions and Nitroxide Free Radicals. J. Am. Chem. Soc. **122** (2000) 718-719.
4. Ise, T.; Ishida, T.; Hashizume, D.; Iwasaki, F.; Nogami. T.: Ferro- and Ferrimagnetic Chains of hin-Bridged Copper(II) and Manganese(II) and hnn-Bridged Manganese(II) Complexes (hin = 4,4,5,5-Tetramethylimidazolin-1-oxyl; hnn = 4,4,5,5-Tetramethylimidazolin-1-oxyl 3-Oxide). Inorg. Chem. **42** (2003) 6106-6113.
5. Lin, H. H.; Mohanta, S.; Lee, C. J.; Wei, H. H.: Syntheses, Crystal Engneering, and Magnetic Property of a Dicyanamide Bridged Three-Dimensional Manganese(II)-Nitronyl Nitroxide Coordination Polymer Derived from a New Radical. Inorg. Chem. **42** (2003) 1548-1553.
6. Wang, L. Y.; Ma, L. F.; Jiang, Z. H.; Liao, D. Z.; Yan.S. P.: Synthesis, crystal structure and magnetic properties of a novel complex Ni(NIT2-thz)$_3$(ClO_4)$_2$. Inorg. Chim. Acta. **358** (2005) 820-823.
7. Jiang, K.; Yang, R. H.; Wang, L. Y.; Wang, Y. F.: Synthesis, Crystal Structure and Magnetic Properties of a New Zn(II)-Nitronyl Nitroxide Complex. Chinese J. Struc. Chem. **27** (2008) 645-650.
8. Li, L. C.; Liao, D. Z.; Jiang, Z. H.: An Unprecedented Asymmetric End-On Azido-Bridged Copper(II) Imino Nitroxide Complex: Structure, Magnetic Properties, and Density Functional Theory Analysis. Inorg. Chem. **45** (2006) 7665-7670.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.