Crystal structure of chloronitrato-2-{2′-[(1′-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxidemercury(II) — mercury(II)chloride, $HgCl(NO_3)(C_{15}H_{19}N_4O_2) \cdot HgCl_2$

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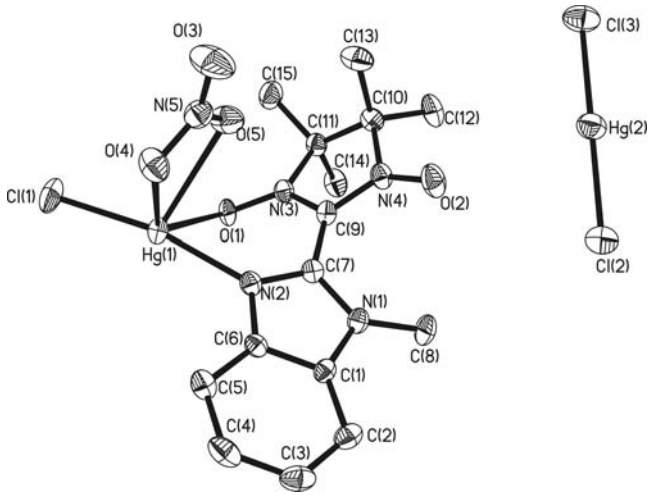

Abstract

$C_{15}H_{19}Cl_3Hg_2N_5O_5$, triclinic, $P\bar{1}$ (no. 2), a = 9.922(2) Å, b = 10.822(2) Å, c = 11.460(2) Å, α = 107.518(2)°, β = 102.046(2)°, γ = 96.639(2)°, V = 1126.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.026, $wR_{ref}(F^2)$ = 0.065, T = 294 K.

Source of material

The nitroxide NIT-1′-MeBzIm (NIT-1′-MeBzIm = 2-{2′-[(1′-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) was prepared by the literature method [1]. To a mixed solution of $Hg(NO_3)_2$ (0.2 mmol) and $HgCl_2$ (0.2 mmol) in ethanol (10 mL) was added with stirring a solution of the NIT-1′-MeBzIm (0.2 mmol) in ethanol (10 mL). The mixture was stirred for further two hours affording a color change from dark purple to dark black, then the reaction mixture was filtered. The filtrate was kept in ether vapor at room temperature by slow diffusion of ether into the ethanol solution of the complex. Black block-shaped single crystal were obtained.

Discussion

During the past decade, nitronyl nitroxide radicals (NITR) have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [2-4], due to their exceptional stability and their rich chemistry. A lot of studies on the magnetic properties of the nitronyl nitroxide and imino nitroxide radicals of metal complexes have been reported [5-7]. In many different types of organic radicals, research was focused on the nitronyl nitroxide radicals (NITR) family because of their flexibility and functionality. Some diamagnetic metal complexes with organic radicals as a ligand, however, have shown ferro or antiferromagnetic interactions operated through the diamagnetic metal ions.

The title crystal structure consists of a Hg(NIT-1′-MeBzIm)(NO_3)(Cl) molecule and a $HgCl_2$ molecule. The distorted square-pyramidal ion Hg1 is coordinated to a NIT-1′-MeBzIm radical ligand, a NO_3^- anion and a Cl^- anion. NIT-1′-MeBzIm radical ligand acting as bidentate chelating ligand coordinates Hg1 ion through the oxygen atom of NIT-1′-MeBzIm and the nitrogen atom of the benzimidazole ring. Three oxygen atoms and one nitrogen atom from the NIT-1′-MeBzIm and NO_3^- anion form the equatorial plane. The chlorine atom occupies axial position. The bond lengths of Hg1—O1, Hg1—O4, Hg1—O5 and Hg1—N2 are 2.593(4) Å, 2.595(4) Å, 2.643(5) Å and 2.111(4) Å, respectively. The axial d(Hg—Cl) is 2.292(2) Å. These values correspond well with those in literatures [8,9]. The bond length O1—N3 (1.284(5) Å) of the coordinated segment is a little longer than the free d(O2—N4) = 1.262(6) Å. O1–N3–C9–N4–O2 is nearly co-planar but make a dihedral angle of 41.0(2)° with the plane of the benzimidazole ring. The approximate linear environment of Hg2 atom is formed by the chlorine atoms. The bond lengths of Hg2—Cl2 and Hg2—Cl3 are 2.265(2) Å and 2.278(2) Å, respectively. The bond angle of Cl2–Hg2–Cl3 is 175.58(8)°. There exit intermolecular interactions, via a weak Hg···O bond with d(Hg1—O1) = 2.938 Å, d(Hg2—O4') = 2.831 Å, d(Hg2—O3') = 2.871 Å. Therefore, formation of a polymeric chain is achieved through intermolecular interactions.

Table 1. Data collection and handling.

Crystal:	black block, size 0.05 × 0.17 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	140.05 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8637, 4162
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3635
$N(param)_{refined}$:	276
Programs:	SHELXS-97, SHELXS-97 [10]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.7407	0.0747	0.1809	0.051
H(3)	2*i*	0.8275	–0.0070	0.0056	0.062
H(4)	2*i*	0.7335	0.0238	–0.1844	0.062
H(5)	2*i*	0.5605	0.1469	–0.2024	0.050
H(8A)	2*i*	0.5288	0.3129	0.3583	0.075
H(8B)	2*i*	0.6623	0.2515	0.3431	0.075
H(8C)	2*i*	0.5185	0.1597	0.3212	0.075
H(12A)	2*i*	0.1099	0.3837	0.4215	0.086
H(12B)	2*i*	0.1007	0.5290	0.4273	0.086
H(12C)	2*i*	0.2474	0.4907	0.4641	0.086
H(13A)	2*i*	0.0281	0.3324	0.0951	0.091
H(13B)	2*i*	–0.0492	0.4030	0.1950	0.091
H(13C)	2*i*	–0.0038	0.2690	0.1950	0.091
H(14A)	2*i*	0.3934	0.7020	0.3181	0.072
H(14B)	2*i*	0.4005	0.6028	0.3936	0.072
H(14C)	2*i*	0.2931	0.6983	0.4066	0.072
H(15A)	2*i*	0.0706	0.6467	0.2279	0.087
H(15B)	2*i*	0.0697	0.5459	0.0966	0.087
H(15C)	2*i*	0.1791	0.6791	0.1545	0.087

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*	0.35138(2)	0.34707(2)	–0.13381(2)	0.0445(1)	0.0367(1)	0.0295(1)	0.00782(9)	0.00688(9)	0.01419(9)
Hg(2)	2*i*	0.14385(3)	0.11741(3)	0.48201(3)	0.0471(2)	0.0549(2)	0.0618(2)	0.0125(1)	0.0194(1)	0.0195(1)
Cl(1)	2*i*	0.2900(2)	0.4462(2)	–0.2828(2)	0.075(1)	0.061(1)	0.0479(9)	0.0028(8)	–0.0041(8)	0.0340(8)
Cl(2)	2*i*	0.3600(2)	0.0660(2)	0.4929(2)	0.053(1)	0.098(2)	0.092(2)	0.026(1)	0.028(1)	0.047(1)
Cl(3)	2*i*	–0.0655(2)	0.1843(2)	0.4829(2)	0.0506(9)	0.056(1)	0.089(1)	0.0162(8)	0.0219(9)	0.0113(9)
O(1)	2*i*	0.3645(4)	0.5271(4)	0.0794(4)	0.056(2)	0.037(2)	0.036(2)	0.009(2)	0.019(2)	0.022(2)
O(2)	2*i*	0.2594(5)	0.2332(4)	0.2827(5)	0.085(3)	0.047(2)	0.073(3)	0.025(2)	0.044(3)	0.036(2)
O(3)	2*i*	–0.0185(6)	0.0592(6)	–0.2284(6)	0.059(3)	0.087(4)	0.086(4)	–0.019(3)	0.025(3)	–0.002(3)
O(4)	2*i*	0.1774(5)	0.1265(4)	–0.2639(4)	0.065(3)	0.050(3)	0.043(2)	–0.001(2)	0.019(2)	0.003(2)
O(5)	2*i*	0.1177(5)	0.2382(5)	–0.0981(4)	0.050(3)	0.068(3)	0.050(3)	0.014(2)	0.015(2)	0.001(2)
N(1)	2*i*	0.5282(5)	0.2262(4)	0.1778(4)	0.042(3)	0.033(2)	0.027(2)	0.006(2)	0.006(2)	0.009(2)
N(2)	2*i*	0.4474(5)	0.2633(4)	–0.0014(4)	0.039(2)	0.032(2)	0.032(2)	0.007(2)	0.013(2)	0.010(2)
N(3)	2*i*	0.3145(5)	0.4735(4)	0.1510(4)	0.039(2)	0.033(2)	0.028(2)	0.006(2)	0.010(2)	0.009(2)
N(4)	2*i*	0.2649(5)	0.3336(4)	0.2483(4)	0.050(3)	0.029(2)	0.041(3)	0.010(2)	0.019(2)	0.014(2)
N(5)	2*i*	0.0887(5)	0.1402(5)	–0.1974(5)	0.047(3)	0.046(3)	0.042(3)	0.008(2)	0.006(2)	0.010(2)
C(1)	2*i*	0.6006(5)	0.1617(5)	0.0924(5)	0.034(3)	0.026(2)	0.034(3)	0.004(2)	0.004(2)	0.012(2)
C(2)	2*i*	0.7057(6)	0.0895(5)	0.1055(6)	0.036(3)	0.038(3)	0.049(4)	0.005(2)	0.001(3)	0.016(3)
C(3)	2*i*	0.7554(6)	0.0405(6)	0.0005(7)	0.039(3)	0.037(3)	0.079(5)	0.011(3)	0.017(3)	0.017(3)
C(4)	2*i*	0.6993(7)	0.0608(6)	–0.1147(7)	0.058(4)	0.036(3)	0.069(5)	0.009(3)	0.038(4)	0.015(3)
C(5)	2*i*	0.5963(6)	0.1331(5)	–0.1266(6)	0.055(4)	0.031(3)	0.043(3)	0.009(3)	0.022(3)	0.012(3)
C(6)	2*i*	0.5473(5)	0.1854(5)	–0.0195(5)	0.033(3)	0.026(2)	0.035(3)	0.002(2)	0.012(2)	0.009(2)
C(7)	2*i*	0.4375(5)	0.2838(5)	0.1170(5)	0.036(3)	0.026(2)	0.031(3)	0.005(2)	0.009(2)	0.007(2)
C(8)	2*i*	0.5624(7)	0.2386(7)	0.3115(5)	0.062(4)	0.059(4)	0.026(3)	0.012(3)	0.004(3)	0.017(3)
C(9)	2*i*	0.3411(6)	0.3630(5)	0.1735(5)	0.043(3)	0.031(3)	0.030(3)	0.008(2)	0.010(2)	0.012(2)
C(10)	2*i*	0.1626(6)	0.4259(5)	0.2716(5)	0.041(3)	0.036(3)	0.038(3)	0.007(2)	0.014(3)	0.009(2)
C(11)	2*i*	0.2312(6)	0.5438(5)	0.2403(5)	0.043(3)	0.036(3)	0.031(3)	0.012(2)	0.014(2)	0.009(2)
C(12)	2*i*	0.1544(8)	0.4605(6)	0.4088(6)	0.085(5)	0.050(4)	0.049(4)	0.013(3)	0.038(4)	0.020(3)
C(13)	2*i*	0.0213(7)	0.3506(7)	0.1808(7)	0.042(4)	0.064(4)	0.068(5)	0.000(3)	0.016(3)	0.011(4)
C(14)	2*i*	0.3394(7)	0.6460(6)	0.3496(6)	0.066(4)	0.037(3)	0.034(3)	0.003(3)	0.017(3)	0.002(3)
C(15)	2*i*	0.1282(7)	0.6100(7)	0.1737(6)	0.070(5)	0.065(4)	0.056(4)	0.031(4)	0.022(4)	0.032(4)

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. Luneau, D.; Rey, P.; Laugier, J.; Fries, P.; Caneschi, A.; Gatteschi, D.; Sessoli, R.: Nitrogen-bonded copper(II)-imino nitroxide complexes exhibiting large ferromagnetic interactions. J. Am. Chem. Soc. **113** (1991) 1245-1251.
4. Ogita, M.; Yamamoto, Y.; Suzuki, T.; Kaizakim, S.: Syntheses, Structures, and Spectroscopic Properties of Cobalt(III) Complexes Containing 3- or 4-Pyridyl-Substituted Nitronyl and Imino Nitroxide Ligands. Eur. J. Inorg. Chem. **4** (2002) 886-894.
5. Wang, L. Y.; Li, L. C.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.: Synthesis, Crystal Structure and Magnetic Properties of A New Thiazolyl-Substituted Nitronyl Nitroxide and Its Copper(II) Complexes. Eur. J. Inorg. Chem. **11** (2004) 2266-2271.
6. Wang, Y. F.; Wang, L. Y.; Ma, L. F.: Synthesis, Crystal Structures and Magnetic Properties of Copper(II) Complexes with Nitronyl Nitroxide Radicals. Z. Anorg. Allg. Chem. **634** (2008) 181-185.
7. Fedin, M. V.; Veber, S. L.; Gromov, I. A.; Ovcharenko, V. I.; Sagdeev, R. Z.; Schweiger, A.; Bagryanskaya, E. G.: Electron Paramagnetic Resonance of Three-Spin Nitroxide-Copper(II)-Nitroxide Clusters Coupled by a Strong Exchange Interaction. J. Phys. Chem. A. **110** (2006) 2315-2317.
8. Lee, C. J.; Huang, C. H.; Wei, H. H.; Liu, Y. H.; Lee, G. H.; Wang, Y.: Crystal structures and magnetic properties of mercury(II) bromide complexes with pyridyl-substituted *N*-oxyl *N'*-oxides (nitonyl nitroxides). J. Chem. Dalton. Trans. (1998) 171-176.
9. Chang, J. L.; Wang, L. Y.; Jiang, K.: Bis[1-hydroxy-4,4,5,5-tetramethyl-2-(1,3-thiazol-2-yl-κN)-2,3-dihydro-1*H*-imidazole-κN^3]dinitratomercury(II). Acta Crystallogr. **E61** (2005) m2100-m2102.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.