Synthesis and crystal structure of a new mercury(II) chlorine complex with nitronyl nitroxides, $C_{15}H_{19}Cl_4Hg_2N_4O_2$

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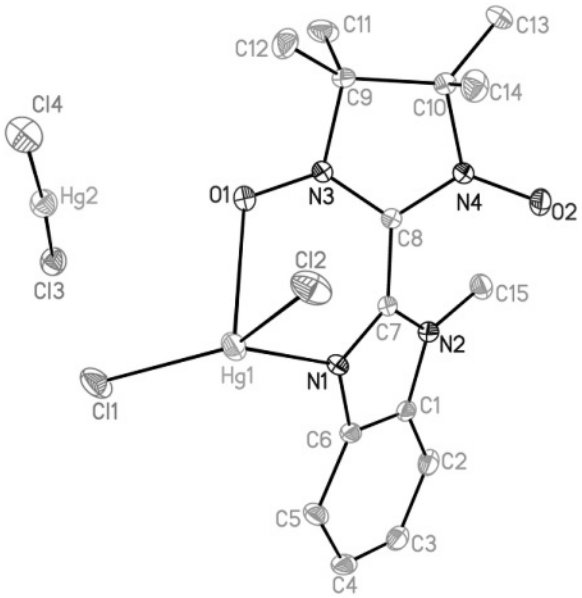

Abstract

$C_{15}H_{19}Cl_4Hg_2N_4O_2$, triclinic, $P\bar{1}$ (no. 2), a = 7.445(2) Å, b = 9.463(2) Å, c = 16.180(3) Å, α = 94.245(2)°, β = 100.747(2)°, γ = 102.523(2)°, V = 1085.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0312, $wR_{ref}(F^2)$ = 0.0815, T = 291 K.

Table 1. Data collection and handling.

Crystal:	black blocks, size 0.18×0.32×0.47 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	146.36 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8239, 3990
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3430
$N(param)_{refined}$:	249
Programs:	SHELX [9]

Source of material

The nitroxide NIT-1'-MeBzIm (NIT-1'-MeBzIm = 2-{2'-[(l'-methyl)benzimidazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) was prepared by the literature method [1]. To the solution of $HgCl_2$ (0.2mmol) in ethanol (10 mL) was added with stirring a solution of the NIT-1'-MeBzIm (0.2mmol) in ethanol (10 mL). The mixture was stirred further five hours affording a color change from purple to black, and then the reaction mixture was filtered. The filtrate was kept in an atmosphere of ether vapor at room temperature. By slow diffusion of ether into the ethanol solution of the complex, block-shaped black single crystals suitable for X-ray analysis were obtained after two weeks.

Discussion

The design and synthesis of multi-dimentional molecule-based magnetic materials is one of the major challenges in molecular materials research [2-3]. Nitronyl nitroxide radicals (NITR), have played a prominent role in the design and construction of molecular magnetic materials, due to their intriguing structural diversity and potential applications. The nitroxide derivatives can be bound to the metal through the oxygen atom of O-N groups, resulting in a good variety of transition metal-radical complexes have been synthesized [4-7]. Nitronyl nitroxide radicals, independently or in combination with metal ions, have been one of the most studied systems in molecular magnetism for understanding the radical-radical or metal-radical interactions as well as for synthesizing organic ferromagnets and metal-radical magnetic materials. In this article, we report the synthesis and crystal structures of a new complex involving nitronyl nitroxide radicals $[HgCl_2(NIT\text{-}MeImz)]\cdot(HgCl_2)$. A perspective view of the molecular structure of $[HgCl_2(NIT\text{-}MeImz)]\cdot(HgCl_2)$ is shown in Figure 1. The compound consists of one discrete four-coordinated Hg(1) complex and one $HgCl_2$ molecule. There are two mercury environments present in the compound, one distorted tetrahedral and one distorted linear structure. Four-coordination of Hg(1) ion is formed by two terminal chlorine atoms [Hg(1)–Cl(1) 2.325(2) Å, Hg(1)–Cl(2) 2.3752(19) Å], one oxygen (O1) and one nitrogen atom (N1) from the NIT-MeImz radical ligand [Hg(1)–N(1) 2.313(5) Å, Hg(1)–O(12) 2.727 Å] in a distorted tetrahedral geometry. Atom Hg(2), originally coordinated by two chlorines, has a linear coordination [Cl(3)–Hg(2)–Cl(4) 176.61(8)°, Hg(2)–Cl(3) 2.3026(19) Å and Hg(2)–Cl(4) 2.280(2) Å]. The fragment O(1)–N(3)–C(8)– N(4)–O(2) is nearly planar, but forms a dihedral angle of 49.248(175)° with the plane of the benzimidazole ring. The coordinated N(3)–O(1) bond length is 1.291(6) Å, which is larger than the uncoordinated N(4)–O(2) bond lengths (1.285(6) Å). The shortest contact distances O(2)···O(2') between atoms belonging to different radical is 7.445 Å, which can be considered as very weak interaction. There exist intermolecular interactions among the crystal, via a weak Hg···Cl bond with Hg(1)···Cl(3) = 3.092 Å, Hg(2)···Cl(2) = 3.140 Å, Hg(2)···Cl(1) = 3.092 Å. Therefore, formation of one dimensional chain is constructed through weak Hg–Cl bonds. The intrachain Hg···Hg separation is 3.916 Å. The π-π piling interactions exist between the nearest neighboring benzimidazole rings which parallel each other with the interplane distance of 3.54 Å, which is in the reported range (3.35 Å - 3.990(9) Å) [8]. The one-dimensional chain structure is connected by π-π piling interactions, and then further to form a 2-D network plane.

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

Atom	Site	x	y	z	U_{iso}
H(2A)	2*i*	0.2187	0.1227	–0.0962	0.054
H(3)	2*i*	0.2464	–0.0758	–0.1837	0.061
H(4)	2*i*	0.2892	–0.2873	–0.1308	0.058
H(5)	2*i*	0.2963	–0.3178	0.0104	0.053
H(11A)	2*i*	–0.0112	0.2396	0.3119	0.088
H(11B)	2*i*	–0.0021	0.2385	0.4094	0.088
H(11C)	2*i*	–0.1063	0.0982	0.3467	0.088
H(12A)	2*i*	0.0913	–0.0421	0.4321	0.086
H(12B)	2*i*	0.2163	0.0947	0.4930	0.086
H(12C)	2*i*	0.3102	–0.0037	0.4407	0.086
H(13A)	2*i*	0.4528	0.4779	0.3857	0.075
H(13B)	2*i*	0.3178	0.4203	0.4458	0.075
H(13C)	2*i*	0.2354	0.4268	0.3500	0.075
H(14A)	2*i*	0.5618	0.1399	0.4031	0.074
H(14B)	2*i*	0.5366	0.2401	0.4796	0.074
H(14C)	2*i*	0.6473	0.3084	0.4131	0.074
H(15A)	2*i*	0.1845	0.2987	0.1235	0.067
H(15B)	2*i*	0.1346	0.2680	0.0244	0.067
H(15C)	2*i*	0.3441	0.3306	0.0717	0.067

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*	0.28823(4)	–0.26264(3)	0.22431(2)	0.0448(2)	0.0325(2)	0.0554(2)	0.0069(1)	0.0091(1)	0.0015(1)
Hg(2)	2*i*	–0.23577(4)	–0.38302(3)	0.27521(2)	0.0515(2)	0.0478(2)	0.0535(2)	0.0150(1)	0.0132(1)	0.0103(1)
Cl(1)	2*i*	0.0442(3)	–0.4685(2)	0.1769(2)	0.050(1)	0.051(1)	0.140(2)	–0.0079(9)	0.035(1)	–0.038(1)
Cl(2)	2*i*	0.5445(3)	–0.1637(2)	0.3397(1)	0.061(1)	0.068(1)	0.061(1)	0.023(1)	–0.0093(9)	–0.014(1)
Cl(3)	2*i*	–0.4200(3)	–0.3817(2)	0.1442(1)	0.056(1)	0.052(1)	0.056(1)	0.0150(8)	0.0130(8)	0.0144(8)
Cl(4)	2*i*	–0.0679(3)	–0.3938(3)	0.4068(1)	0.076(1)	0.068(1)	0.061(1)	0.023(1)	–0.000(1)	0.007(1)
O(1)	2*i*	0.0596(6)	–0.0916(5)	0.2662(3)	0.044(2)	0.033(2)	0.046(3)	0.001(2)	0.014(2)	0.001(2)
O(2)	2*i*	0.5017(7)	0.3231(5)	0.2472(3)	0.061(3)	0.047(3)	0.045(3)	–0.016(2)	0.022(2)	–0.003(2)
N(1)	2*i*	0.2838(7)	–0.0901(5)	0.1303(3)	0.036(2)	0.028(2)	0.033(2)	0.003(2)	0.009(2)	–0.005(2)
N(2)	2*i*	0.2519(7)	0.1177(5)	0.0795(3)	0.033(2)	0.032(3)	0.032(2)	0.005(2)	0.009(2)	0.001(2)
N(3)	2*i*	0.1685(7)	0.0375(5)	0.2852(3)	0.037(2)	0.026(2)	0.034(2)	0.004(2)	0.011(2)	0.001(2)
N(4)	2*i*	0.3795(7)	0.2344(6)	0.2767(3)	0.044(3)	0.029(3)	0.035(2)	0.001(2)	0.016(2)	–0.002(2)
C(1)	2*i*	0.2533(8)	0.0214(7)	0.0115(4)	0.027(3)	0.037(3)	0.030(3)	–0.001(2)	0.008(2)	–0.001(2)
C(2)	2*i*	0.2379(9)	0.0374(8)	–0.0747(4)	0.041(3)	0.052(4)	0.034(3)	–0.006(3)	0.008(2)	0.006(3)
C(3)	2*i*	0.2529(9)	–0.0820(9)	–0.1262(4)	0.042(3)	0.064(4)	0.034(3)	–0.013(3)	0.011(3)	–0.012(3)
C(4)	2*i*	0.2774(9)	–0.2111(9)	–0.0940(4)	0.037(3)	0.057(4)	0.043(3)	–0.002(3)	0.010(3)	–0.022(3)
C(5)	2*i*	0.2850(9)	–0.2300(8)	–0.0099(4)	0.039(3)	0.039(3)	0.048(3)	0.005(3)	0.007(3)	–0.013(3)
C(6)	2*i*	0.2745(8)	–0.1077(7)	0.0441(4)	0.029(3)	0.037(3)	0.033(3)	0.002(2)	0.008(2)	–0.006(2)
C(7)	2*i*	0.2723(8)	0.0457(6)	0.1485(4)	0.031(3)	0.027(3)	0.031(3)	0.002(2)	0.010(2)	0.000(2)
C(8)	2*i*	0.2706(8)	0.1075(6)	0.2343(4)	0.035(3)	0.027(3)	0.032(3)	0.004(2)	0.012(2)	0.001(2)
C(9)	2*i*	0.1818(8)	0.1304(7)	0.3673(4)	0.038(3)	0.037(3)	0.029(3)	0.004(2)	0.012(2)	–0.003(2)
C(10)	2*i*	0.3601(8)	0.2553(7)	0.3677(4)	0.040(3)	0.033(3)	0.032(3)	0.004(2)	0.012(2)	0.002(2)
C(11)	2*i*	–0.0015(9)	0.1814(9)	0.3580(5)	0.037(4)	0.070(5)	0.062(5)	0.008(3)	0.013(3)	–0.025(4)
C(12)	2*i*	0.202(1)	0.0360(9)	0.4401(4)	0.064(5)	0.062(5)	0.034(3)	–0.011(4)	0.013(3)	0.008(3)
C(13)	2*i*	0.340(1)	0.4092(7)	0.3893(5)	0.062(4)	0.033(4)	0.052(4)	0.006(3)	0.020(3)	–0.012(3)
C(14)	2*i*	0.5436(9)	0.2340(8)	0.4209(4)	0.036(3)	0.056(4)	0.050(4)	0.004(3)	0.001(3)	0.006(3)
C(15)	2*i*	0.227(1)	0.2666(7)	0.0743(4)	0.044(4)	0.036(4)	0.053(4)	0.007(3)	0.009(3)	0.005(3)

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