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Inorganic Chemistry Communications 10 (2007) 1444–1447

INORGANIC CHEMISTRY COMMUNICATIONS

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Synthesis, structure and magnetic properties of a novel lead(II) complex containing nitronyl nitroxide radicals

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Received 27 June 2007; accepted 21 August 2007
Available online 5 September 2007

Abstract

The lead(II) complex with nitronyl nitroxide, $[Pb(NIT2Py)_2(NO_3)_2]$ [NIT2Py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide], has been prepared and characterized by magnetic and single-crystal X-ray diffraction studies. In the complex, the lead(II) ion is coordinated with two bidentate nitronyl nitroxide and two nitrate anions. The lead(II) ion shows seven-coordinate geometry. Magnetic susceptibility data for the title complex has been measured in the range 5–300 K. There are antiferromagnetic interaction between the coordinated nitronyl nitroxides ($J = -19.35\ \mathrm{cm^{-1}}$) and intermolecular ferromagnetic interactions. Thus, we observe the sixth periodic IVA group metal element Pb(II) ion providing an effective pathway for the magnetic exchange interaction between nitronyl nitroxide radicals.

Keywords: Nitronyl nitroxide; Lead; Magnetic properties; Crystal structure

The design and synthesis of magnetic materials is an attracting research area. Nitronyl nitroxide radicals (NITR), stable organic radicals, have played a prominent role in the design and construction of molecular magnetic materials [1,2]. There have been a lot of studies on the magnetic properties of the nitronyl nitroxide and imino nitroxide radicals of metal complexes which have been reported [3–10]. Some diamagnetic metal complexes with organic radicals as a ligand, however, have shown ferro- or antiferromagnetic interactions are operative through the diamagnetic metal ions. Oshio et al. [11] have reported that a copper(I) ion in $[Cu^I(im\text{-}mepy)_2](PF_6)$ (immepy = 4,4,5,5-teramethyl-2-(6′-methyl-2′-pyridyl)imidazoline-1-oxyl) mediates rather strong intramolecular ferromagnetic interaction between the coordinated radicals. They have also reported the diamagnetic Cu(I) and Ag(I) complexes with imino nitroxide [12,13]. The results revealed that the copper(I) complexes with imino nitroxide radicals exhibited an intramolecular ferromagnetic interaction between the coordinated radicals through the diamagnetic Cu(I) ion, however, in solid state the silver(I) complexes with imino nitroxide exhibit a weak antiferromagnetic coupling. Zhang et al. [14] reported on the magnetic studies of a silver(I) complex of nitronyl nitroxide which also exhibited a fairly strong antiferromagnetic interaction through the Ag(I) ion. Hg(II) complex of nitronyl nitroxide has a weak antiferromagnetic interaction through the Hg^{2+} ion [15]. However, according to our knowledge, study of main-group metal complexes with nitronyl nitroxides has been lacking so far. Therefore, we report here the synthesis, structure, and magnetic properties of lead(II) complex with nitronyl nitroxide radicals, $[Pb(NIT2Py)_2(NO_3)_2]$. In addition, we also observe that the main-group metal element Pb(II) ion provides an effective pathway for the magnetic exchange interaction between nitronyl nitroxide radicals.

The radical ligand, 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT2Py) was prepared according to the literature method [16,17]. The complex $[Pb(NIT2Py)_2(NO_3)_2]$ was synthesized by the adding $Pb(NO_3)_2$

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doi:10.1016/j.inoche.2007.08.022

(0.041 g, 0.125 mmol) to a 20 mL ethanol solution of NIT2Py (0.061 g, 0.25 mmol). The mixture was stirred for 14 h and then filtered; the clear dark blue filtrate was diffused with diethyl ether vapour at room temperature in the dark for three weeks. Black crystals were obtained in a yield of 46%. Anal. calcd. for $C_{24}H_{32}PbN_8O_{10}$: C 36.01, H 4.03, N 14.01. Found C 36.10, H 4.07, N 13.99. IR: $\nu_{N\text{–}O}$ (1374.29 cm^{-1}).

An ORTEP drawing of the title complex is shown in Fig. 1. In the complex, Pb(II) ion [18] is coordinated to two nitrogen atoms of two radical ligands, two oxygen atoms from two uniform radical ligands and three oxygen atoms from nitrate anions. The NIT2Py chelates via pyridyl-N and nitroxide-O atoms to a Pb(II) center in the complex, and occurs a severe distortion. The Pb(II) ion is chelated by O atoms and N atoms of NIT2Py with a Pb–N distance of 2.862(2), 2.730(2) Å and a Pb–O distance of 2.528(2), 2.591(2) Å, and also O atoms of nitrate anions with a Pb–O distance of 2.631(3), 2.714(3), 2.763(4) Å, which are in the normal range [19,20]. The coordination environments observed in the complex is seven-coordinated (four of NIT2Py ligand, three of nitrate anions). The coordinated N–O length [N3–O2 = 1.294(3), N6–O4 = 1.294(3) Å] is longer than the uncoordinated N–O length [N2–O1 = 1.276(3), N5–O3 = 1.275(3) Å], as is generally observed [21,22]. The angles between the pyridyl ring and the nitroxide group for the two different NIT2Py radicals are 24.8° and 30.8°, respectively.

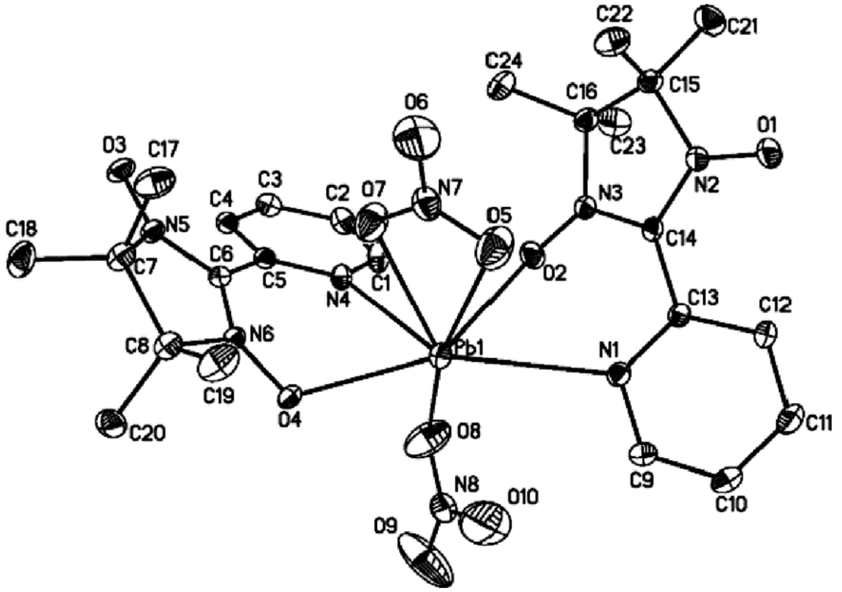

Fig. 1. ORTEP view of the complex $[Pb(NIT2Py)_2(NO_3)_2]$. Selected bond distances (Å): Pb(1)–O(2) 2.591(2), Pb(1)–O(7) 2.631(3), Pb(1)–O(5) 2.714(3), Pb(1)–N(4) 2.730(2), Pb(1)–O(8) 2.763(4), Pb(1)–N(1) 2.862(2), Pb(1)–N(4) 2.730(2), N(3)–O(2) 1.294(3), N(6)–O(4) 1.294(3), N(2)–O(1) 1.276(3), N(5)–O(3) 1.275(3). Selected bond angles (°): O(5)–Pb(1)–O(8) 165.12(13), O(4)–Pb(1)–O(7) 76.03(8), N(4)–Pb(1)–O(8) 71.84(9), O(2)–Pb(1)–O(7) 86.52(10), O(4)–Pb(1)–N(1) 155.48(7), O(2)–Pb(1)–O(5) 77.28(10), O(4)–Pb(1)–N(4) 66.97(6), O(4)–Pb(1)–N(1) 155.48(7).

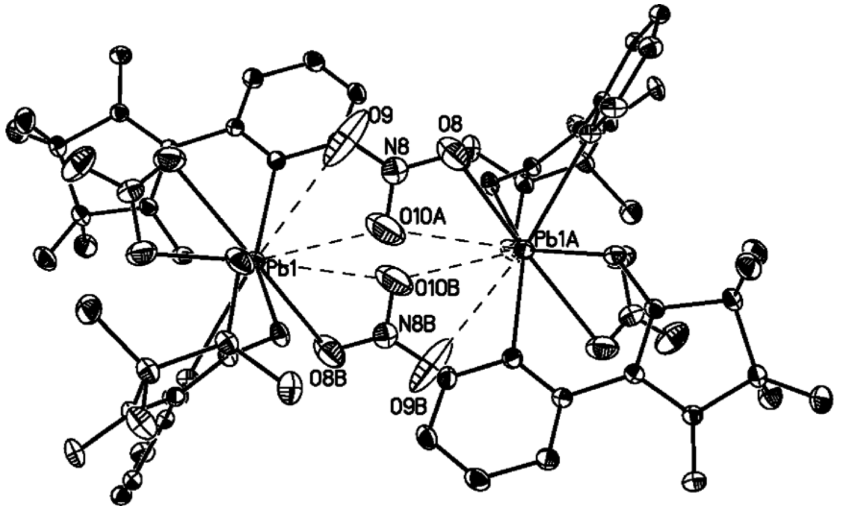

Fig. 2. Dimer structure of the complex $[Pb(NIT2Py)_2(NO_3)_2]$.