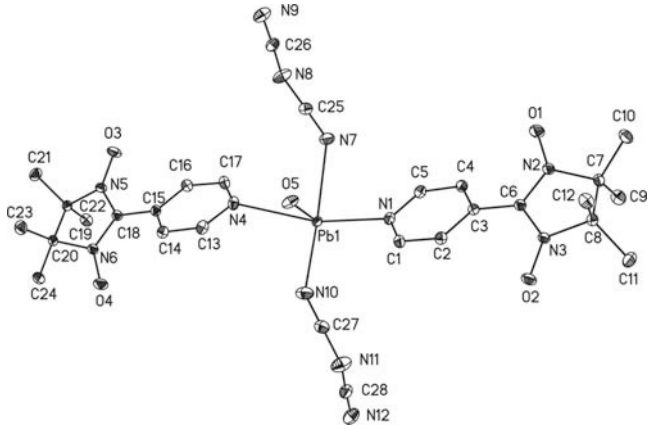
Crystal structure of monoaqua-[2-(4-pyridyl)-4,4,5,5,-tetramethylimidazoline-1-oxyl-3-oxide]-dicyanamidolead(II), $Pb(H_2O)(C_{12}H_{16}N_3O_2)_2(C_2N_3)_2$

Yu-Fang Wang, Yong-Hua Zhang and Li-Ya Wang*

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, P. R. China

Received Juli 6, 2009, accepted and available on-line September 9, 2009; CCDC no. 1267/2702



Abstract

$C_{28}H_{34}N_{12}O_5Pb$, triclinic, $P\bar{1}$ (no. 2), a = 7.1782(5) Å, b = 13.693(1) Å, c = 17.596(1) Å, α = 108.367(1)°, β = 93.901(1)°, γ = 101.398(1)°, V = 1593.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.017, $wR_{ref}(F^2)$ = 0.041, T = 291 K.

Source of material

The nitronyl nitroxide radical, 2-(4-pyridyl)-4,4,5,5,-tetramethylimidazoline-1-oxyl-3-oxide (NITpPy), was prepared according to the literature method [1]. The title compound was synthesized by adding $Na[N(CN)_2]$ (0.045 g, 0.5 mmol) to 20 mL of an ethanol solution containing $Pb(NO_3)_2$ (0.083 g, 0.25 mmol) and NITpPy (0.125 g, 0.5 mmol). The mixture was stirred for 8 h at room temperature and then filtered off; the black filtrate was allowed to stand at room temperature. Black crystals suitable for X-ray analysis were obtained after two weeks.

Discussion

The syntheses of new molecular magnetic materials that combine metal ions and organic radicals as ligating sites have attracted much more attention in the last few years [2-4]. Stable Nitronyl nitroxide radicals (NITR), have played a prominent role in the design and construction of molecular magnetic materials. These nitroxide radicals are especially attractive due to their donor atoms and to their ability to assemble extended coordination geometry with changing magnetic coupling. The "metal-organic" strategy of combining pyridyl-substituted nitronyl nitroxide with metal has been reported successfully [5-7]. The dicyanamide anion $[N(CN)_2]^-$ can act as a terminal ligand, it can act as a bridging ligand [8,9].

In the title crystal structure lead(II) atom is five-coordinated in a distorted square-pyramidal environment, in which the basal sites are occupied by four nitrogen atoms (N1, N4, N7, N10), with the bond lengths of 2.556(2), 2.705(2), 2.611(2), and 2.515(3) Å, respectively. The axial position is occupied by oxygen atom (O5) from water molecule, with the bond length of 2.409(2) Å. The dihedral angle between the pyridyl ring and ON–C–NO moieties is 23.16°. The shortest distance between the two N–O groups from NITpPy is 3.633 Å. In the complex, the $[N(CN)_2]^-$ anions act as terminal ligands. N–Pb–N angles significantly deviate from orthogonal, ranging from 81.76(7)° to 94.51(9)°. The Pb(II) ion has a displacement of 0.631 Å out of the basal plane. In addition, the C25–N8–C26 and C27–N11–C28 angles are 122.7(3)° and 120.6(3)°, respectively, indicating the pseudo C_{2v} symmetry of the dicyanamide groups [10]. There exist two kind of the intermolecular interaction. The hydrogen bonds of O–H···N type have been observed between the hydrogen atom from the coordinated water molecule and the nitrogen atom from the dicyanamide anion (2.799 Å for N9B···O5K, 2.902 Å for N8M···O5K). There is another weak interaction between the molecules *via* the Pb ions and nitrogen atoms from the dicyanamide anion (2.918 Å for Pb1C···N12L, 3.609 Å for Pb1A···N11B). Thus the units of $[Pb(NITpPy)_2(N(CN)_2)_2(H_2O)]$ were connected in a two-dimensional network by the double intermolecular H bonds and double weak interactions by the lead atoms.

Table 1. Data collection and handling.

Crystal:	black block, size 0.19 × 0.26 × 0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	53.53 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12032, 5912
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5649
$N(param)_{refined}$:	431
Programs:	SHELXS-97 [11], SHELXL-97 [12], SHELXTL [13]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.4358	1.1416	0.2940	0.038
H(2)	2*i*	0.3746	1.3056	0.3145	0.035
H(4)	2*i*	0.9427	1.4313	0.3802	0.036
H(5)	2*i*	0.9857	1.2626	0.3550	0.036
H(9A)	2*i*	0.7355	1.6643	0.5189	0.065
H(9B)	2*i*	0.7453	1.7820	0.5250	0.065

* Correspondence author (e-mail: wlya@lynu.edu.cn)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(9C)	2*i*	0.9181	1.7308	0.4991	0.065
H(10A)	2*i*	0.9026	1.7834	0.3796	0.061
H(10B)	2*i*	0.7134	1.8240	0.3907	0.061
H(10C)	2*i*	0.7254	1.7337	0.3113	0.061
H(11A)	2*i*	0.2297	1.6600	0.4476	0.065
H(11B)	2*i*	0.3859	1.7657	0.4683	0.065
H(11C)	2*i*	0.4122	1.6833	0.5105	0.065
H(12A)	2*i*	0.4393	1.5959	0.2696	0.057
H(12B)	2*i*	0.3820	1.7032	0.3105	0.057
H(12C)	2*i*	0.2423	1.5959	0.3030	0.057
H(13)	2*i*	0.5487	0.7505	0.1523	0.042
H(14)	2*i*	0.5668	0.5767	0.1152	0.038
H(16)	2*i*	1.1399	0.6782	0.1808	0.037
H(17)	2*i*	1.1014	0.8483	0.2165	0.042

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(21A)	2*i*	1.0608	0.2961	–0.0184	0.066
H(21B)	2*i*	1.0862	0.2172	0.0273	0.066
H(21C)	2*i*	1.2465	0.3201	0.0429	0.066
H(22A)	2*i*	1.2474	0.3880	0.1864	0.060
H(22B)	2*i*	1.0956	0.2878	0.1852	0.060
H(22C)	2*i*	1.0578	0.4008	0.2237	0.060
H(23A)	2*i*	0.5595	0.2644	–0.0013	0.066
H(23B)	2*i*	0.7241	0.2064	–0.0280	0.066
H(23C)	2*i*	0.7443	0.3237	–0.0250	0.066
H(24A)	2*i*	0.7612	0.2646	0.1874	0.062
H(24B)	2*i*	0.7594	0.1705	0.1084	0.062
H(24C)	2*i*	0.5777	0.2177	0.1223	0.062
H(1W)	2*i*	0.510(2)	0.993(3)	0.157(2)	0.06(1)
H(2W)	2*i*	0.667(4)	0.964(3)	0.125(1)	0.07(1)

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}
Pb(1)	2*i*	0.79220(1)	1.004253(7)	0.294350(5)	0.03057(6)	0.02572(6)	0.02384(6)	0.00958(4)	0.00797(4)	0.00874(4)
O(1)	2*i*	0.9135(3)	1.5795(2)	0.3411(2)	0.032(1)	0.044(1)	0.080(2)	0.0091(9)	0.025(1)	0.024(1)
O(2)	2*i*	0.3073(3)	1.4670(2)	0.4006(1)	0.031(1)	0.039(1)	0.078(2)	0.0088(8)	0.024(1)	0.030(1)
O(3)	2*i*	1.1847(3)	0.5162(2)	0.0865(1)	0.035(1)	0.039(1)	0.077(2)	0.0098(8)	0.026(1)	0.030(1)
O(4)	2*i*	0.5808(3)	0.4221(2)	0.1558(2)	0.033(1)	0.044(1)	0.081(2)	0.0104(9)	0.028(1)	0.021(1)
O(5)	2*i*	0.6155(3)	0.9797(2)	0.1657(1)	0.039(1)	0.066(1)	0.029(1)	0.024(1)	0.0102(9)	0.019(1)
N(1)	2*i*	0.7157(3)	1.1860(2)	0.3229(1)	0.036(1)	0.028(1)	0.027(1)	0.0107(9)	0.0046(9)	0.0074(9)
N(2)	2*i*	0.7514(3)	1.5800(2)	0.3665(1)	0.023(1)	0.029(1)	0.039(1)	0.0057(8)	0.0082(9)	0.0123(9)
N(3)	2*i*	0.4587(3)	1.5252(2)	0.3890(1)	0.024(1)	0.027(1)	0.038(1)	0.0060(8)	0.0094(9)	0.0149(9)
N(4)	2*i*	0.8215(3)	0.8165(2)	0.1900(1)	0.045(1)	0.027(1)	0.032(1)	0.013(1)	0.002(1)	0.0076(9)
N(5)	2*i*	1.0319(3)	0.4623(2)	0.1009(1)	0.029(1)	0.028(1)	0.039(1)	0.0083(8)	0.0116(9)	0.0158(9)
N(6)	2*i*	0.7400(3)	0.4162(2)	0.1281(1)	0.026(1)	0.026(1)	0.039(1)	0.0059(8)	0.0079(9)	0.0097(9)
N(7)	2*i*	1.0566(4)	1.0847(2)	0.2221(2)	0.042(1)	0.055(2)	0.044(1)	0.010(1)	0.016(1)	0.018(1)
N(8)	2*i*	1.2516(4)	1.0197(3)	0.1168(2)	0.050(2)	0.093(2)	0.040(1)	0.041(2)	0.017(1)	0.031(1)
N(9)	2*i*	1.2432(4)	1.0317(2)	–0.0195(2)	0.065(2)	0.075(2)	0.038(2)	0.030(2)	0.018(1)	0.021(1)
N(10)	2*i*	0.4461(4)	0.9401(2)	0.3068(2)	0.040(1)	0.076(2)	0.046(2)	–0.002(1)	0.008(1)	0.022(1)
N(11)	2*i*	0.2179(5)	0.9801(3)	0.4018(2)	0.069(2)	0.098(2)	0.056(2)	0.037(2)	0.026(2)	0.038(2)
N(12)	2*i*	0.2123(5)	0.9491(2)	0.5322(2)	0.074(2)	0.073(2)	0.036(2)	0.022(2)	0.015(1)	0.010(1)
C(1)	2*i*	0.5382(4)	1.2006(2)	0.3113(2)	0.034(1)	0.026(1)	0.031(1)	0.005(1)	0.002(1)	0.007(1)
C(2)	2*i*	0.4999(3)	1.2990(2)	0.3237(2)	0.026(1)	0.031(1)	0.032(1)	0.009(1)	0.002(1)	0.010(1)
C(3)	2*i*	0.6518(3)	1.3882(2)	0.3501(1)	0.027(1)	0.027(1)	0.027(1)	0.007(1)	0.005(1)	0.009(1)
C(4)	2*i*	0.8378(3)	1.3737(2)	0.3624(2)	0.026(1)	0.029(1)	0.031(1)	0.005(1)	0.003(1)	0.007(1)
C(5)	2*i*	0.8618(4)	1.2720(2)	0.3475(2)	0.029(1)	0.034(1)	0.029(1)	0.012(1)	0.001(1)	0.009(1)
C(6)	2*i*	0.6200(3)	1.4946(2)	0.3668(2)	0.025(1)	0.027(1)	0.033(1)	0.0058(9)	0.006(1)	0.011(1)
C(7)	2*i*	0.6916(4)	1.6809(2)	0.4074(2)	0.033(1)	0.024(1)	0.028(1)	0.005(1)	0.003(1)	0.008(1)
C(8)	2*i*	0.4695(4)	1.6384(2)	0.3935(2)	0.032(1)	0.025(1)	0.030(1)	0.009(1)	0.007(1)	0.010(1)
C(9)	2*i*	0.7809(4)	1.7179(2)	0.4958(2)	0.046(2)	0.044(2)	0.034(2)	0.001(1)	–0.004(1)	0.012(1)
C(10)	2*i*	0.7650(4)	1.7631(2)	0.3687(2)	0.046(2)	0.032(1)	0.044(2)	0.001(1)	0.006(1)	0.018(1)
C(11)	2*i*	0.3646(4)	1.6918(2)	0.4612(2)	0.047(2)	0.044(2)	0.041(2)	0.020(1)	0.015(1)	0.009(1)
C(12)	2*i*	0.3745(4)	1.6328(2)	0.3116(2)	0.038(1)	0.039(2)	0.039(2)	0.007(1)	–0.002(1)	0.017(1)
C(13)	2*i*	0.6682(4)	0.7353(2)	0.1589(2)	0.037(1)	0.037(1)	0.033(1)	0.018(1)	0.001(1)	0.011(1)
C(14)	2*i*	0.6773(4)	0.6305(2)	0.1362(2)	0.030(1)	0.033(1)	0.032(1)	0.009(1)	0.002(1)	0.008(1)
C(15)	2*i*	0.8570(4)	0.6071(2)	0.1454(2)	0.033(1)	0.024(1)	0.028(1)	0.008(1)	0.005(1)	0.009(1)
C(16)	2*i*	1.0179(4)	0.6909(2)	0.1753(2)	0.029(1)	0.032(1)	0.034(1)	0.008(1)	–0.001(1)	0.013(1)
C(17)	2*i*	0.9931(4)	0.7929(2)	0.1965(2)	0.040(2)	0.027(1)	0.034(1)	0.004(1)	–0.001(1)	0.008(1)
C(18)	2*i*	0.8761(3)	0.4977(2)	0.1250(2)	0.027(1)	0.026(1)	0.034(1)	0.007(1)	0.007(1)	0.011(1)
C(19)	2*i*	1.0137(4)	0.3497(2)	0.0994(2)	0.034(1)	0.024(1)	0.031(1)	0.010(1)	0.008(1)	0.010(1)
C(20)	2*i*	0.7914(4)	0.3124(2)	0.0886(2)	0.035(1)	0.023(1)	0.029(1)	0.005(1)	0.006(1)	0.008(1)
C(21)	2*i*	1.1107(4)	0.2903(2)	0.0316(2)	0.050(2)	0.041(2)	0.046(2)	0.022(1)	0.017(1)	0.012(1)
C(22)	2*i*	1.1128(4)	0.3573(2)	0.1813(2)	0.039(2)	0.041(2)	0.043(2)	0.008(1)	–0.001(1)	0.019(1)
C(23)	2*i*	0.6959(4)	0.2730(2)	0.0003(2)	0.047(2)	0.043(2)	0.035(2)	0.004(1)	–0.003(1)	0.010(1)
C(24)	2*i*	0.7154(4)	0.2341(2)	0.1305(2)	0.049(2)	0.030(1)	0.046(2)	0.004(1)	0.010(1)	0.018(1)
C(25)	2*i*	1.1410(4)	1.0551(2)	0.1690(2)	0.029(1)	0.045(2)	0.034(1)	0.008(1)	0.003(1)	0.016(1)
C(26)	2*i*	1.2394(4)	1.0285(2)	0.0443(2)	0.035(2)	0.046(2)	0.037(2)	0.017(1)	0.009(1)	0.011(1)
C(27)	2*i*	0.3463(4)	0.9577(2)	0.3554(2)	0.039(2)	0.049(2)	0.038(2)	0.001(1)	0.002(1)	0.018(1)
C(28)	2*i*	0.2223(5)	0.9620(2)	0.4716(2)	0.048(2)	0.044(2)	0.040(2)	0.010(1)	0.011(1)	0.004(1)

Acknowledgments. This work was supported by the National Natural Science Foundation of China (grant no. 20771054) and the Natural Science Foundation of Henan Province (grant no. 0311021200).

References

1. Ullman, E. F.; Osiechi, J. H.: Stable free radicals: Nitronyl nitroxide monoradicals and biradicals as possible small molecule spin labels. J. Am. Chem. Soc. **94** (1972) 7049-7059.
2. Luneau, D.; Risoan, G.; Rey, P.; Grand, A.; Caneschi, A.; Gatteschi, D.; Lugier, J.: Transition Metal Derivatives of a Chelating Nitronyl Nitroxide Ligand. Nickel(II) and Manganese(II) Complexes. Inorg. Chem. **32** (1993) 5616-5622.
3. Oshio, H.; Watanabe, T.; Ohto, A.; Ito, T.; Nagashima, U.: Farirly Strong Ferromagnetic Interactions between Imino Nitroxide Ligands through a Diamagentic CuI Ion in $[CuI(im\text{-}mepy)_2](PF_6)$. Angew. Chem., Int. Ed. **33** (1994) 670-671.
4. Yamamoto, Y.; Suzuki, T.; Kaizaki, S.: Crystal structures, magnetic and spectroscopic properties of manganese(II), cobalt(II), nickel(II) and zinc(II) dichloro complexes bearing two 2-pyridyl-substituted imino nitroxides. J. Chem. Soc. Dalton Trans. (2001) 1566-1572.
5. Fettouhi, M.; Khaled, M.; Waheed, A.; Golhen, S.; Ouahab, L.; Sutter, J. P.; Kahn, O.: Manganese(II) Coordination Complexes Complexes Involving Nitronyl Nitroxide Radicals. Inorg. Chem. **38** (1999) 3967-3971.
6. 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 (nitronyl nitroxides). J. Chem. Dalton. Trans. (1998) 171-176.
7. 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.
8. Lin, H. H.; Mohanta, S.; Lee, C. J.; Wei, H. H.: Systheses, Crystal Engineering, and Magnetic Property of a Dicyanamide Bridged Three-Dimensional Manganese(II)-Nitronyl Nitoxide Coordination Polymer Derived from a New Radical. Inorg. Chem. **42** (2003) 1548-1553.
9. Yeung, W. F.; Gao, S.; Wong, W. T.; Lau, T. C.: Antiferromagnetic ordering in a novel five-connected 3D polymer $SV2(2,5\text{-}Me_2pyz)[N(CN)_2]_{4n}$ ($2,5\text{-}Me_2pyz = 2,5$-dimethylpyrazine). New J. Chem. **26** (2002) 523-525.
10. Dasna, I.; Golhen, S.; Ouahab, L.;Fettouhi, M.; Pena, O.; Daro, N.; Sutter, J. P.: Synthesis, X-ray crystal structures and magnetic properties of $Cu(II)(NITpPy)_2[N(CN)_2]_2 \cdot solv$ (NITpPy = nitronyl nitroxide radical, $solv = H_2O$ or CH_3CN). From discrete molecules to 2-D polymeric coordination compounds. Inorg. Chim. Acta **326** (2001) 37-46.
11. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
12. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
13. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.