Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5493-5494

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14474

NOTE

Synthesis and Crystal Structure of Diaqua*bis*(3,5-di(3-pyridyl)-1*H*-1,2,4-triazole)cobalt(II) Diformate

RUI CHEN[1], LINI HUO[2,*], YANFANG LIAO[3] and FU PING HUANG[4,*]

[1]College of Chinese Medical Science, Guangxi University of Chinese Medicine, Nanning 530001, P.R. China
[2]College of Pharmcy, Guangxi University of Chinese Medicine, Nanning 530001, P.R. China
[3]Guangxi Research Institute of Chemical Industry, Nanning 530001, P.R. China
[4]Department of Chemistry, Guangxi Normal University, Guilin 5410004, P.R. China

*Corresponding authors: Tel: +86 15994365816; E-mail: huolini@126.com; 75973229@qq.com

(*Received*: 24 August 2012; *Accepted*: 15 April 2013) AJC-13239

A novel complex daqua*bis*(3,5-di(3-pyridyl)-1*H*-1,2,4-triazole)cobalt(II) diformate synthesized with a formula as $[Co(C_{12}H_8N_5)_2(H_2O)_2(HCOO)_2]$, was synthesized by 3,5-di(3-pyridyl)-1*H*-1,2,4-triazole (3-1*H* -bpt) and $Co(HCOO)_2{\cdot}2H_2O$. In the crystal structure of the present complex, the Co(II) atom is coordinated by two N atoms from two monodentate 3-1*H*-bpt ligands. The crystal packing is consolidated by intermolecular O-H---N, O-H---O and N-H---O hydrogen bonds. The crystal is monoclinic, space group $P2_1/n$ with unit cell parameters: a = 7.29917 (11) Å, b = 11.45053 (16) Å, c = 16.1982 (2) Å, α = 90º, β = 95.8367 (14), γ = 90º, V = 1346.82 (3)Å^3, Z = 2, M_r = 631.48, D_c = 1.557 g/cm^3, μ = 0.70 mm^{-1}, $F_{(000)}$ = 650, R = 0.0288, wR (F^2) = 0.0729 for 2519 reflections with $I > 2\sigma(I)$.

Key Words: Complex, Crystal structure, 3,5-Di(3-pyridyl)-1*H*-1,2,4-triazole.

The coordination chemistry of 1,2,4-triazole and its derivatives ligands has generated considerable recent interest for the construction of various metal coordination polymers[1-3]. 3-N-Donor analogue of 3-4H-bpt, is of further interest due to its potential tendency to show three typical conformations under appropriate surroundings[4]. And 3,5-di(3-pyridyl)-1*H*-1,2,4-triazole (3-1H-bpt) ligands have not been reported yet. So we present here the crystal structure of the title compound (Fig. 1), a new Co(II) complex with the 3-1*H*-bpt and formate ligands.

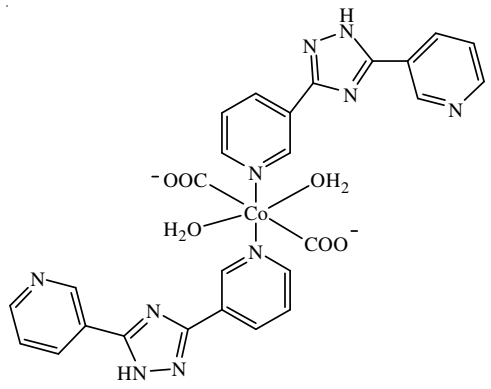

Fig. 1

The mononuclear unit of the title compound, $[Co(C_{12}H_8N_5)_2(H_2O)_2(HCOO)_2]$, the Co(II) atom is coordinated by two N atoms from two monodentate 3,5-di(3-pyridyl)-1*H*-1,2,4-triazole (3-1*H* -bpt) ligands (Fig. 1), two O atoms from two formate anions and two water molecules. In the crystal, the Co(II) ion adopts a linear coordination geometry [N-Co-N = 180.00] with the two ligands bound to the metal atom *via* the 3-pyridine N atoms. The crystal packing is consolidated by intermolecular O-H---N, O-H---O and N-H---O hydrogen bonds.

All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. 3,5-Di(3-pyridyl)-1*H*-1,2,4-triazole (3-1*H*-bpt) ligands was prepared by similar procedure reported in the literature[5]. Analyses for carbon, hydrogen and nitrogen were performed on a Agilent SuperNova analyzer.

Synthesis: A mixture of 3-1*H* -bpt (11.9 mg, 0.05 mmol), $Co(HCOO)_2{\cdot}2H_2O$ (14.8 mg, 0.10 mmol), water (10 mL) and ethanol (10 mL) was sealed in a reaction vessel. The reaction vessel was then sealed and subsequently placed in an oven for 72 h at 160 ºC well shaped red block crystals were obtained and washed with ethanol.

Crystal structure determination: A single crystal of compound with dimensions of 0.45 mm × 0.35 mm × 0.21 mm was selected for crystallographic data collection at 293(2)

K and structure determination on a Agilent Xcalibur diffractometer employing graphite-monochromated MoK_α radiation (λ = 0.7107 Å). A total of 7510 reflections were collected in the range of 5.92° ≤ θ ≤ 52.74°, of which 2741 reflections were unique with R_{int} = 0.017. The data were collected using CrysAlisPro and reduced by the program CrysAlisPro. All the structures were solved by direct methods and refined by full-matrix least squares method on 'F^2_{obs}' by using SHELXS97 software package. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 202 variable parameters for 2519 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.029$ and $wR^2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.1731$ (2) where $w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.5729P$ and $P = (F_o^2 + 2F_c^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.254 and -0.264 e/Å^3, respectively.

The bond lengths and bond angles are given in Table-1 and All hydrogen bond patterns are given in Table-2. Fig. 2 shows the molecular structure of the present compound. Fig. 3 shows the packing diagram of the present compound. In the mononuclear complex, the equatorial site of Co(II) center is occupied by two formate anions and two aqua molecules while the axial site is occupied by two nitrogen atoms of two monodentate 3-1*H*-bpt ligands. The axial Co-N distances [2.2062(13) Å] are significantly longer than those of the Co-O equatorial lengths [2.0752(11) and 2.0748(12) Å]. The coordinating N1 and N1A atoms are on the same side of the molecule and the N-Co-N angle [180.00 (6)°] is 180°. In the structure, 3-1*H*-bpt molecule exhibits trans-conformation and the two terminal pyridyl groups and the bridging triazole heterocyclic ring almost lie in the same plane. The torsion angles for the two pyridyl rings are -0.1(3) (C6-C5-C7-N2) and 179.95(18)° (C8-C9-C10-N5). Viewed from the whole crystal structure, each complex is linked together by intermolecular O-H…O hydrogen bonds from H_2O and carboxyl of 3-1*H*-bpt to form a supramolecular.

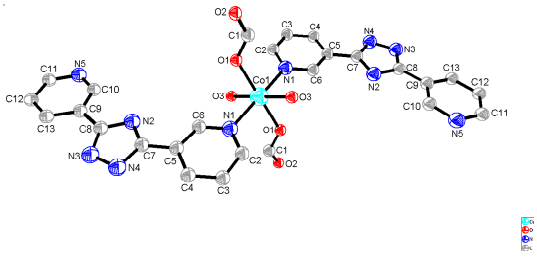

Fig. 2. Molecular structure of the title compound

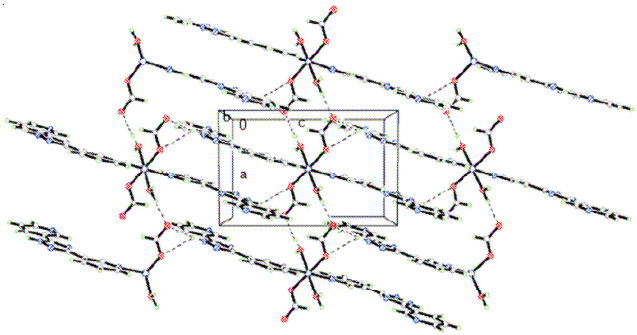

Fig. 3. A perspective view of the two-dimensional hydrogen-bonded net along the plane

TABLE-1
BOND DISTANCES (Å) AND ANGLES (°)

Co1–O1	2.0752(11)	N4–C7	1.324(2)
Co1–O1A	2.0752(11)	C–N5	1.334(3)
Co1–O3A	2.0748(12)	C–C12	1.368(3)
Co1–O3	2.0748(12)	C2–C3	1.380(2)
Co1–N1	2.2062(13)	C3–C4	1.374(3)
Co1–N1A	2.2062(13)	C4–C5	1.389(2)
O1–C1	1.242(2)	C5–C6	1.388(2)
O2–C1	1.241(2)	C5–C7	1.467(2)
N1–C2	1.341(2)	C8–C9	1.464(2)
N1–C6	1.337(2)	C9–C10	1.382(2)
N2–C7	1.357(2)	C9–C13	1.386(2)
N2–C8	1.328(2)	C10–N5	1.330(2)
N3–N4	1.353(2)	C12–C13	1.382(3)
N3–C8	1.338(2)	–	–
O1A–Co1–O1	180.0	N5–C–C12	122.56(18)
O1–Co1–N1A	89.72(5)	O2–C1–O1	125.72(16)
O1–Co1–N1	90.28(5)	N1–C2–C3	123.19(16)
O1A–Co1–N1	89.72(5)	C4–C3–C2	118.84(16)
O1A–Co1–N1A	90.28(5)	C3–C4–C5	119.34(16)
O3A–Co1–O1A	88.29(5)	C4–C5–C7	121.61(15)
O3–Co1–O1A	91.71(5)	C6–C5–C4	117.76(15)
O3A–Co1–O1	91.71(5)	C6–C5–C7	120.61(15)
O3–Co1–O1	88.29(5)	N1–C6–C5	123.62(15)
O3A–Co1–O3	180.00(7)	N2–C7–C5	123.48(15)
O3–Co1–N1	89.69(5)	N4–C7–N2	114.76(15)
O3A–Co1–N1A	89.69(5)	N4–C7–C5	121.72(15)
O3–Co1–N1A	90.31(5)	N2–C8–N3	109.59(15)
O3A–Co1–N1	90.31(5)	N2–C8–C9	125.48(15)
N1A–Co1–N1	180.00(6)	N3–C8–C9	124.93(15)
C1–O1–Co1	125.85(11)	C10–C9–C8	119.24(16)
C2–N1–Co1	120.31(11)	C10–C9–C13	117.27(17)
C6–N1–Co1	122.42(11)	C13–C9–C8	123.48(16)
C6–N1–C2	117.23(14)	N5–C10–C9	123.80(18)
C8–N2–C7	102.98(14)	C10–N5–C	117.97(17)
C8–N3–N4	110.53(14)	C–C12–C13	119.13(19)
C7–N4–N3	102.14(14)	C12–C13–C9	119.25(17)

TABLE-2
HYDROGEN BOND DISTANCES (Å)

D–H···A	D–H	H···A	D···A	D–H···A
O3–H3···N5^{i}	0.86 (3)	1.86 (2)	2.729 (2)	176 (2)
O3–H3···O2^{ii}	0.85 (3)	1.86 (2)	2.691 (2)	167 (2)
N3–H3···O2^{iii}	0.86	2.01	2.858 (2)	170 (4)

Symmetry codes: (i) x+1/2, -y+5/2, -z+1/2; (ii) - x+1, y, z; (iii) x, y+1, z.

ACKNOWLEDGEMENTS

The authors thank the Guangxi Administration of Traditional Chinese Medicine (Grant No. gzzc1208), the Subject for College of Chinese Medical Science (Grant No. 2012zr01) for financial support.

REFERENCES

1. H.J. Chen, Z.W Mao, S. Gao and X.M. Chen, *Chem. Commun.*, 2320 (2001).
2. J.G. Haasnoot, *Coord. Chem. Rev.*, **131**, 200 (2000).
3. J.J. Liu, X. He, M. Shao and M.X. Li, *J. Mol. Struc.*, **919**, 189 (2009).
4. M. Du, Zhi, H. Zhang, Y.P. You and X.J. Zhao, *Cryst. Eng. Commun.*, **10**, 306 (2008).
5. L.L. Liu and G. Yang, Molbank., M563, doi:10.3390/M563 (2008).