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New bidentate ligand 2-(1-(naphthalen-2-ylmethyl)-1H-pyrazol-3-yl)pyridine: Synthesis, characterization and x-ray crystal structure

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ABSTRACT

New ligand 2-(1-(naphthalen-2-ylmethyl)-1H-pyrazol-3-yl)pyridine (L^{2naph}) has been synthesised and its structure confirmed by X-ray crystallography. The L^{2naph} ligand containing one arm of pyrazolyl-pyridine connected to a naphthyl unit, the ligand potentially bidentate and crystallized in symmetry cell setting monoclinic of P2(1)/c.

KEYWORDS

3-(2-yridyl)pyrazole;
Coordination chemistry;
Crystal structure.

INTRODUCTION

Synthesis and design multi-dentate ligand based on bis and more 3-(2-pyridyl)pyrazole arms in coordination chemistry has attracted a great interest in supramolecular 3-(2-pyridyl) pyrazole coordination chemistry due to the various structures of the final product[1-3]. Word and co-worker have been interested to study the coordination behaviour of this type of ligands based on deferent spacers which permit several different coordination modes such as M_8L_{12}, M_6L_9, M_4L_6[1g]. The one arm ligands based on 3-(2-pyridyl)pyrazole exhibits a systematic structural variation of coordination architectures. Therefore, the selection of proper ligands is play an important role in the structure of complex, for example 2,2-bipyridine and 3-(2-pyridyl)pyrazole which are very similar in structure have been well used in the synthesis of functional complexes. In this paper, we describes the synthesis, crystal structure of 2-(1-(naphthalen-2-ylmethyl)-1H-pyrazol-3-yl)pyridine ligand.

EXPERIMENTAL

3-(2-Pyridyl)pyrazole was synthesized by reported procedures[4]. All the other reagents for synthesis were commercially available and used as received.

Synthesis of the ligand

A mixture of 2-(bromomethyl)naphthalene (0.50 g, 1.76 mmol), 3-(2-pyridyl)pyrazole (0.256 g, 1.76 mmol), aqueous NaOH (10 M, 10 mL) and tetrahydrofuran (THF) (50 mL) was heated at reflux with stirring for 24 h. After cooling, the organic layer was washed with water and then dried over MgSO4. Removal of the solvent in vacuo afforded pale yellow oil which afforded a white powder on recrystallization from CH_2Cl_2–Et_2O (0.37g, 74%). ES-MS mass spectrum: m/z 286 (100%). ^{1}H NMR (250 MHz, $CDCl_3$): 5.87(2 H, s, CH2), 8.56 (1 H, d, pyridyl H6), 7.18(1 H, t, pyridyl H5), 7.45(1H, t, pyridyl H4), 7.23 (1 H, d, pyridyl H3), 7.07 (1 H, d, pyazolyl H5), 6.80 (1 H, d, pyrazolyl H4), 7.18(1H,d, naphthyl H3), 7.94-8.01(2H,

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m, naphthyl H4, H5, H8), 7.46(1H, d, naphtyl, 1H), 7.55-7.58(2H, m, naphthyl, H6, H7). ES mass spectrum: m/z 286 (MH+). X-ray quality crystals were grown by slow diffusion of diethyl ether vapour into a concentrated CH_2Cl_2 solution of ligand.

RESULTS AND DISCUSSION

The ligand syntheses (Figure 1 for structural formulas) used standard method reactions of 1 equiv of 3-(2-pyridyl)pyrazole with 2-(bromomethyl) naphthalene, under basic conditions to deprotonate the pyrazole. For coordination, the ligand contained one bidentate pyrazolyl-pyridine units (TABLE 1). However, the pyridine N-atom is externally directed, away from the pyrazolyl-pyridine bridging sites (Figure 1) as reported previously[4].

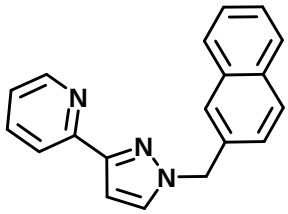

Figure 1 : Structure of the ligand.

The ligand L^{2naph} (Figure 2) was fully characterised by ^1H NMR spectroscopy, mass spectrometry (see experimental) and an X-ray crystal structure has determined (TABLE 2).

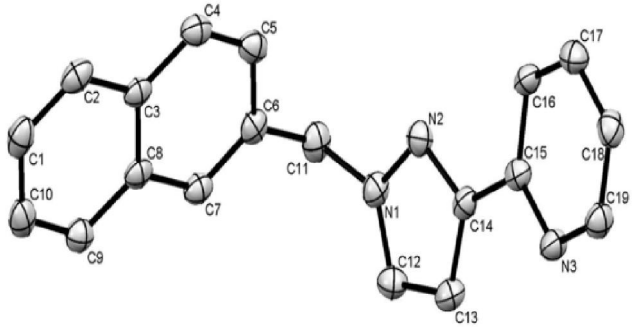

Figure 2 : Crystal structure of the ligand showing the numbering of atoms, hydrogen atoms are omitted for clarity.

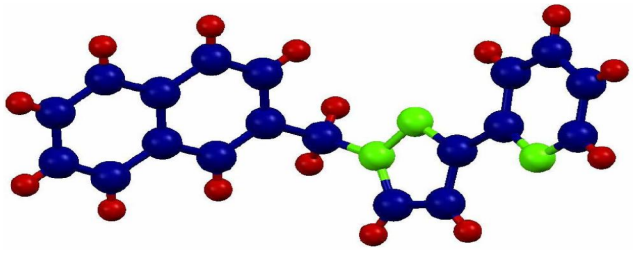

Figure 3 : Crystal structure shows the arrangement of the pyrazolyl-pyridine.

In conclusion, new ligand based on one arm of pyrazolylpyridine linked to naphthalene spacer has been synthesised and its complexes with Cu (II), Zn (II), Ni (II), Cd (II), and Ag (I) under investigations.

TABLE 1 : Selected bond lengths [Å] and angles [°] for the ligand.

N(1)-C(12)	1.350(2)	C(12)-N(1)-C(11)	128.52(16)
N(1)-N(2)	1.353(2)	N(2)-N(1)-C(11)119.41(15)	109.02(18)
N(1)-C(11)	1.457(2)	C(4)-C(3)-C(2)	122.68(17)
C(2)-C(3)	1.427(3)	C(1)-C(2)-C(3)	120.71(18)
N(3)-C(19)	1.338(2)	C(19)-N(3)-C(15)	117.35(15)

TABLE 2 : Crystal data and structure refinement for the ligand.

Formula	C19 H15 N3
Fw	285.34
T(K)	100(2)
λ (Å)	0.71073
Crystal syst.	Monoclinic, P2(1)/c
a (Å)	16.0832(15)
b (Å)	7.5901(7)
c (Å)	11.8509(10)
α (deg)	90
β (deg)	91.255(6)
γ (deg)	90
V(Å^3)	1446.3(2)
Z	4
D_{calcd} (Mg/m^3)	1. 310
M (mm^{-1})	0.079
Crystal size (mm)	0.30 x 0.26 x 0.08
Data / restraints / param	3230 / 0 / 199
Goodness-of-fit on F^2	1.055
R1, wR2	0.0521, 0.1363

SUPPLEMENTARY MATERIAL

Crystalographic data for the structural analysis has been deposited with the Cambridge Crystalographic Data Centre as supplementary publication. CCDC 923559. Copies of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 01223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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