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# Synthesise, Charactrization and Crystal Structure Determination of Pyridine Carboxaldehyde Schiff bases

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## Abstract:

**In this reserch the crystalline Schiff-base compounds ABN-4=$L_1$ (ABN-4: 4-pyridine carboxaldehyde and 4-Hydroxybenzhydrazide ) and ABN-25=$L_2$ (ABN-25: 2-pyridine carboxaldehyde and 1,2-diphenyldihydrazide) was synthesized from condensation of 2- pyridine carboxaldehyde with 4-Hydroxybenzhydrazide and 1,2-diphenyldihydrazide respectively in methanol or ethanol as solvent. The crystals of these compounds that are bright yellow or clear yellow were investigated with FT-IR, X-ray, UV-Vis and elemental analysis.**

**Keywords: Crystal structure, Pyridine, Hydrazide**

## Introduction:

The structure of graphite was determined from single-crystal diffraction in 1924 by two groups independently. Hull also used the powder method to determine the structures of various metals, such as iron and magnesium [1].

Because of catalytic and liquid crystal properties and their similarity with enzimes, Schiff base ligands and their complexes with transition metals are noticed by the scientits. In recent years the exsistence of vanadium compounds in the body of sea animals were argumented by the biochemists [2]. Becase of the importance of Schiff base ligands and their complexes, our purpose in this reserch was synthesis and study of hydrazide Schif base and their complexes with vanadium[3].

## Experimental:

Tridentate Schiff base ligands ($L_1$ and $L_2$ ) were synthesized from the condensation of 4-Hydroxybenozhydrazide and 4-pyridine carboxaldehyde and and 1,2-diphenyldihydrazide with 2- pyridine carboxaldehyde, respectively, in methanol or ethanol as solvent. After refluxing of amine and aldehyde for 7- 8 hours the ligands were obtained. Solution of ligands was wite for ligand $L_1$ and brown for ligand $L_2$. After filteration of the solutions of ligands, suitable crystals of them were obtained from the recrystalized in the mixture of absolute ethanol and n-hexane.

## Results and discussion:

Some physical characterization of these ligands are summarized in table 1.

Table 1: Some Physical Properties of Ligand and its Complex

| Compound | Molecular Weight | Yield% | Melting Point | Color |
|---|---|---|---|---|
| Ligand ABN-4 | 241 | 90 | 168 | wite |
| Ligand ABN-25 | 314 | 95 | 70 | yellow |

In figurs 1, 2 and 3 molecular struture of ligand $L_1$ (4-Hydroxybenzhydrazide with 4- pyridine carboxaldehyde), unit cell and geometry of hydrogene bond of $L_1$ ligand are showed. As shown in figure 1 two molecules of $L_1$ are standing opposite to each other.

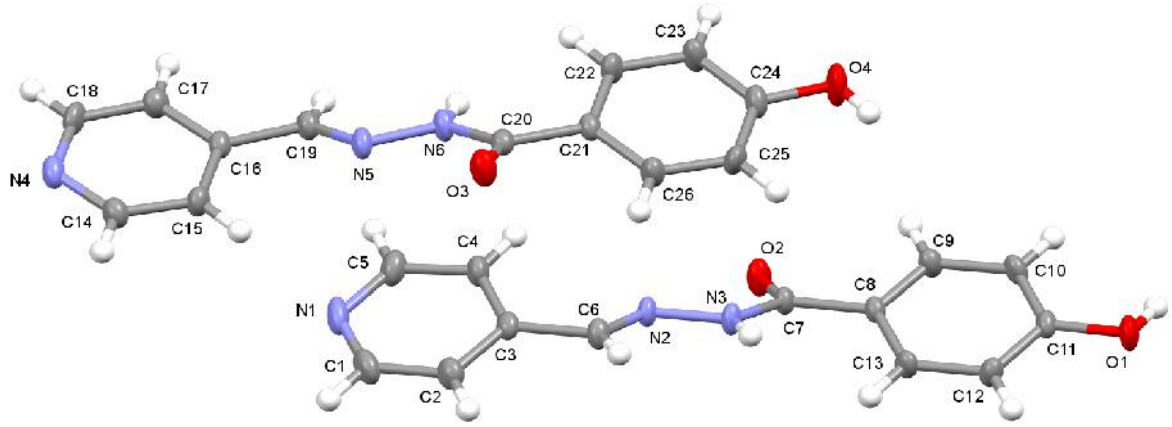


Figure1: Molecular stucture of the tow of ligand $L_1$

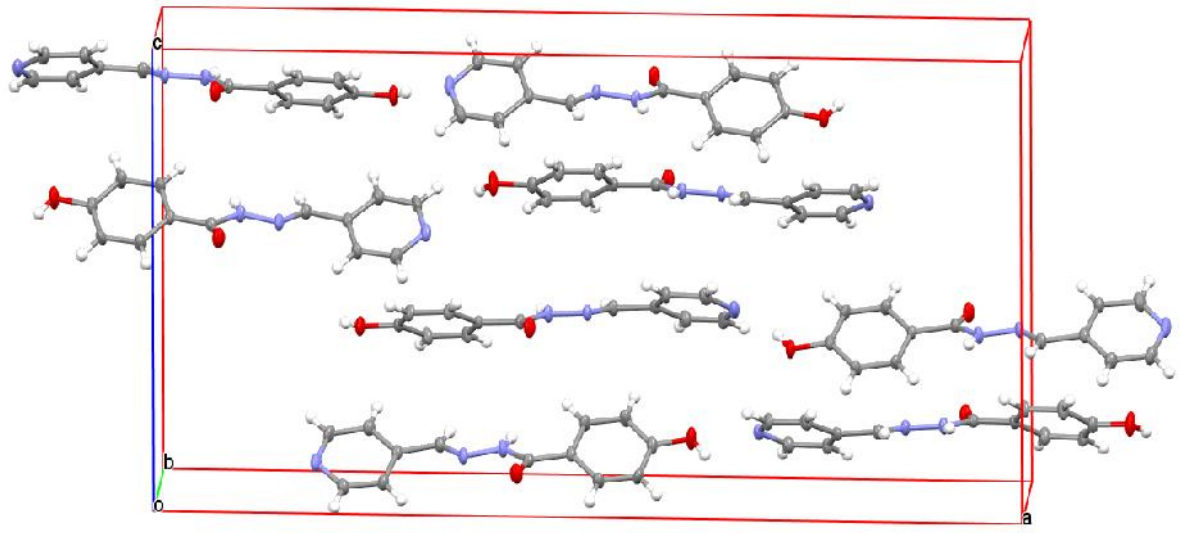


Figure2: Unit cell packing of ligand $L_1$

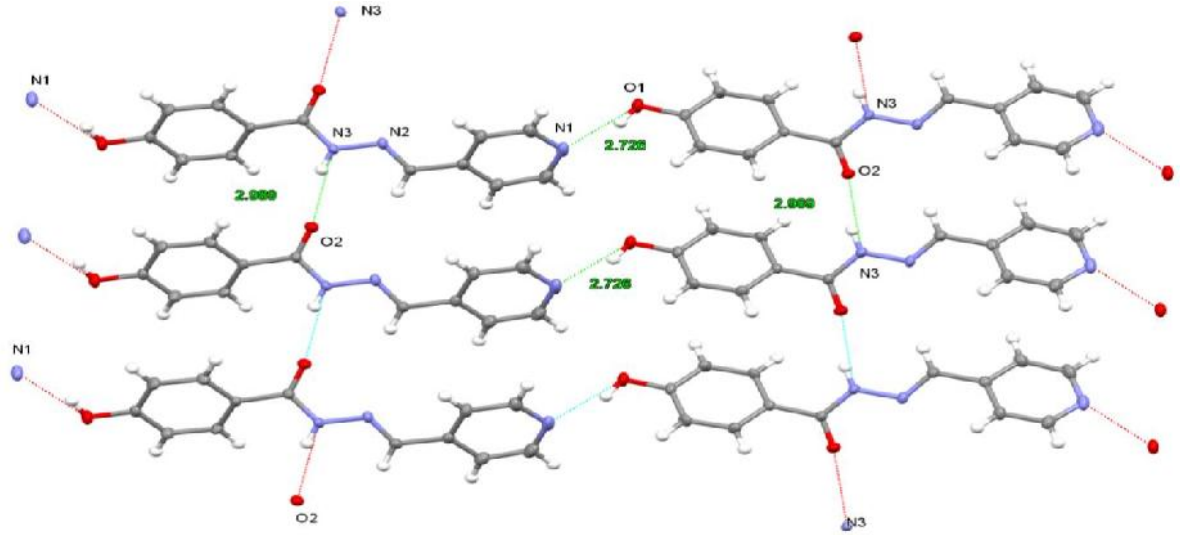


Figure3: The geometry of Hydrogen bond of ligand ($L_1$=ABN-4)

Tables 1, 2 and 3, are showing fractional atomic coordinates and isotropic temperature factors (Angstrom squared), with standard deviations in the least significant digits in parentheses. For anisotropic atoms, thee equivalent isotropic temperature factors (tabble1), and the complete listing of bond ditances (table2) and complete listing of bond angles (degrees) (table3) are shown.

Table 1
Fractional atomic coordinates and isotropic temperature factors
(Angstrom squared). $L_1$=ABN-4

| | X | Y | Z | U(eq) |
|---|---|---|---|---|
| O(2) | 0.43068(7) | 0.24768(40) | 0.38675(20) | 0.04602 |
| O(1) | 0.23034(7) | 0.69236(47) | 0.34285(19) | 0.04839 |
| H(1) | 0.21490 | 0.57095 | 0.36096 | 0.07258 |
| O(3) | 0.57897(7) | 1.26553(39) | 0.61722(20) | 0.04877 |
| N(5) | 0.64441(8) | 0.90807(47 | 0.62053(21) | 0.03616 |
| N(6) | 0.59940(8) | 0.84350(46) | 0.63151(20) | 0.03674 |
| H(6) | 0.59131 | 0.68570 | 0.64150 | 0.04409 |
| N(3) | 0.44714(8) | 0.67554(46) | 0.37705(20) | 0.03476 |
| H(3) | 0.43746 | 0.83237 | 0.37149 | 0.04172 |
| N(2) | 0.49295(8) | 0.62362(47) | 0.38525(20) | 0.03404 |
| O(4) | 0.38349(7) | 0.74461(48) | 0.65080(24) | 0.06436 |
| H(4) | 0.36689 | 0.84911 | 0.62585 | 0.09654 |
| N(4) | 0.81367(9) | 0.93189(55) | 0.60442(20) | 0.04286 |
| N(1) | 0.66205(10) | 0.63010(59 | 0.39626(24) | 0.05053 |
| C(16) | 0.72187(10) | 0.79008(52) | 0.61579(22) | 0.03110 |
| C(12) | 0.29678 | 0.79922(60) | 0.31372(23) | 0.03782 |
| H(12) | 0.29678 | 0.94189 | 0.28178 | 0.04539 |
| C(21) | 0.51939(9) | 0.95457(53) | 0.63242(23) | 0.03180 |
| C(22) | 0.50568(11) | 0.74034(60) | 0.68072(26) | 0.04055 |
| H(22) | 0.52736 | 0.64079 | 0.70980 | 0.04866 |

| | | | | |
|---|---|---|---|---|
| C(20) | 0.56768(10 | 1.03852(55) | 0.62604(22) | 0.03314 |
| C(6) | 0.52033(10 | 0.81434(54) | 0.37889(24) | 0.03540 |
| H(6A) | 0.50977 | 0.98221 | 0.36912 | 0.04248 |
| C(8) | 0.36842(9) | 0.53928(52) | 0.36917(21) | 0.02792 |
| C(7) | 0.41758(10) | 0.47243(54) | 0.37798(22) | 0.03094 |
| C(13) | 0.35283(10) | 0.75238(59) | 0.32261(23) | 0.03561 |
| H(13) | 0.37373 | 0.86507 | 0.29706 | 0.04273 |
| C(3) | 0.56958(10) | 0.75840(60) | 0.38767(24) | 0.03336 |
| C(4) | 0.58427(11) | 0.54384(66) | 0.43435(24) | 0.04093 |
| H(4) | 0.56343 | 0.43883 | 0.46351 | 0.04912 |
| C(9) | 0.33674(11) | 0.37458(60) | 0.40628(24) | 0.03763 |
| H(9) | 0.34674 | 0.23028 | 0.43736 | 0.04516 |
| C(11) | 0.27527(10) | 0.63490(58) | 0.35213(21) | 0.03260 |
| C(15) | 0.73528(10) | 1.00763(62) | 0.56984(23) | 0.03935 |
| H(15) | 0.71372 | 1.11096 | 0.54196 | 0.04722 |
| C(17) | 0.75575(11) | 0.64131(62) | 0.65404(24) | 0.04184 |
| H(17) | 0.74829 | 0.49080 | 0.68439 | 0.05021 |
| C(19) | 0.67329(10) | 0.72479(58) | 0.62775(24) | 0.03635 |
| H(19) | 0.66408 | 0.55588 | 0.64013 | 0.04362 |
| C(14) | 0.78099(11) | 1.06999(66) | 0.56574(25) | 0.04282 |
| H(14) | 0.78948 | 1.21658 | 0.53424 | 0.05138 |
| C(18) | 0.80076(11) | 0.71860(66) | 0.64669(27) | 0.04606 |
| H(18) | 0.82315 | 0.61638 | 0.67259 | 0.05527 |
| C(23) | 0.46018(11) | 0.67407(64) | 0.68591(27) | 0.04620 |
| H(23) | 0.45122 | 0.53153 | 0.71899 | 0.05545 |
| C(2) | 0.60216(11) | 0.91222(67) | 0.34851(25) | 0.04544 |

Table 2: Complete listing of bond distances (Angstroms). $L_1$=ABN-4

| | | | |
|---|---|---|---|
| O(2) - C(7) | 1.226(4) | O(1) - H(1) | 0.820(3) |
| O(1) - C(11) | 1.356(4) | O(3) - C(20) | 1.222(4) |
| N(5) - N(6) | 1.370(4) | N(5) - C(19) | 1.272(4) |
| N(6) - H(6) | 0.860(3) | N(6) - C(20) | 1.370(4) |
| N(3) - H(3) | 0.860(3 | N(3) - N(2) | 1.374(4) |
| N(3) - C(7) | 1.358(4) | N(2) - C(6) | 1.271(4) |
| O(4) - H(4) | 0.820(3) | O(4) - C(24) | 1.362(4) |
| N(4) - C(14) | 1.332(5) | N(4) - C(18) | 1.330(5) |
| N(1) - C(1) | 1.328(6) | N(1) - C(5) | 1.334(5) |
| C(16) - C(15) | 1.380(5) | C(16) - C(17) | 1.384(5) |
| C(16) - C(19) | 1.474(5) | C(12) - H(12) | 0.930(4) |
| C(12) - C(13) | 1.378(5) | C(12) - C(11) | 1.383(5) |
| C(21) - C(22) | 1.388(5) | C(21) - C(20) | 1.482(4) |
| C(21) - C(26) | 1.383(5) | C(22) - H(22) | 0.930(4) |
| C(22) - C(23) | 1.378(5) | C(6) - H(6A) | 0.930(3) |
| C(6) - C(3) | 1.477(5) | C(8) - C(7) | 1.487(4) |
| C(8) - C(13) | 1.386(5) | C(8) - C(9) | 1.380(5) |
| C(3) - C(2) | 1.378(5) | C(4) - H(4) | 0.930(4) |
| C(4) - C(5) | 1.380(5) | C(9) - H(9) | 0.930(4) |
| C(9) - C(10) | 1.387(5) | C(11) - C(10) | 1.382(5) |
| C(15) - H(15) | 0.930(4) | C(15) - C(14) | 1.378(5) |

| | | | |
|---|---|---|---|
| C(17) - H(17) | 0.930(4) | C(17) - C(18) | 1.382(5) |
| C(19) - H(19) | 0.930(4) | C(14) - H(14) | 0.930(4) |
| C(18) - H(18) | 0.930(4) | C(23) - H(23) | 0.930(4) |
| C(23) - C(24) | 1.383(5) | C(2) - H(2) | 0.930(4) |
| C(2) - C(1) | 1.387(5 | C(1) - H(1) | 0.930(4) |
| C(5) - H(5) | 0.930(4) | C(10) - H(10) | 0.930(4) |
| C(24) - C(25) | 1.367(5) | C(26) - H(26) | 0.930(4) |
| C(26) - C(25) | 1.378(5) | C(25) - H(25) | 0.930(4) |

Table 3: Complete listing of bond angles (degrees). $L_1$=ABN-4

| | | | |
|---|---|---|---|
| H(1)-O(1)-C(11) | 109.5(3) | N(6)-N(5)-C(19) | 116.7(3) |
| N(5)-N(6)-H(6) | 121.1(3) | N(5)-N(6)-C(20) | 117.8(3) |
| H(6)-N(6)-C(20) | 121.1(3) | H(3)-N(3)-N(2) | 120.9(3) |
| H(3)-N(3)-C(7) | 120.9(3) | N(2)-N(3)-C(7) | 118.2(3) |
| N(3)-N(2)-C(6) | 117.3(3) | H(4)-O(4)-C(24) | 109.5(3) |
| C(14)-N(4)-C(18) | 117.0(3) | C(1)-N(1)-C(5) | 116.9(4) |
| C(15)-C(16)-C(17) | 117.5(3) | C(15)-C(16)-C(19) | 121.6(3) |
| C(17)-C(16)-C(19) | 120.9(3) | H(12)-C(12)-C(13) | 119.9(4) |
| H(12)-C(12)-C(11) | 119.9(3) | C(13)-C(12)-C(11) | 120.3(3) |
| C(22)-C(21)-C(20) | 122.9(3) | C(22)-C(21)-C(26) | 118.6(3) |
| C(20)-C(21)-C(26) | 118.6(3) | C(21)-C(22)-H(22) | 119.8(4) |
| C(21)-C(22)-C(23) | 120.5(4) | H(22)-C(22)-C(23) | 119.8(4) |
| O(3)-C(20)-N(6) | 121.6(3) | O(3)-C(20)-C(21) | 123.0(3) |
| N(6)-C(20)-C(21) | 115.4(3) | N(2)-C(6)-H(6A) | 121.3(3) |
| N(2)-C(6)-C(3) | 117.3(3) | H(6A)-C(6)-C(3) | 121.4(3) |
| C(7)-C(8)-C(13) | 123.3(3) | C(7)-C(8)-C(9) | 118.1(3) |
| C(13)-C(8)-C(9) | 118.5(3) | O(2)-C(7)-N(3) | 121.9(3) |
| O(2)-C(7)-C(8) | 122.1(3) | N(3)-C(7)-C(8) | 116.0(3) |
| C(12)-C(13)-C(8) | 120.8(3) | C(12)-C(13)-H(13) | 119.6(4) |
| C(8)-C(13)-H(13) | 19.6(3) | C(6)-C(3)-C(4) | 120.4(3) |
| C(6)-C(3)-C(2) | 121.6(3) | C(4)-C(3)-C(2) | 117.9(3) |
| C(3)-C(4)-H(4) | 120.6(4) | C(3)-C(4)-C(5) | 118.9(4) |
| H(4)-C(4)-C(5) | 120.6(4) | C(8)-C(9)-H(9) | 119.4(4) |
| C(8)-C(9)-C(10) | 21.2(3) | H(9)-C(9)-C(10) | 119.4(4) |
| O(1)-C(11)-C(12) | 118.0(3) | O(1)-C(11)-C(10) | 122.4(3) |
| C(12)-C(11)-C(10) | 119.6(3) | C(16)-C(15)-H(15) | 120.4(3) |
| C(16)-C(15)-C(14) | 119.3(3) | H(15)-C(15)-C(14) | 120.4(4) |
| C(16)-C(17)-H(17) | 120.3(4) | C(16)-C(17)-C(18) | 119.4(4) |
| H(17)-C(17)-C(18) | 120.3(4) | N(5)-C(19)-C(16) | 117.5(3) |
| N(5)-C(19)-H(19) | 121.2(3) | C(16)-C(19)-H(19) | 121.3(3) |
| N(4)-C(14)-C(15) | 123.6(4) | N(4)-C(14)-H(14) | 118.2(4) |
| C(15)-C(14)-H(14) | 118.2(4) | N(4)-C(18)-C(17) | 123.3(4) |
| N(4)-C(18)-H(18) | 118.4(4) | C(17)-C(18)-H(18 | 118.4(4) |
| C(22)-C(23)-H(23) | 120.0(4) | C(22)-C(23)-C(24) | 120.0(4) |
| H(23)-C(23)-C(24) | 120.0(4) | C(3)-C(2)-H(2) | 120.5(4) |
| C(3)-C(2)-C(1) | 119.0(4) | H(2)-C(2)-C(1) | 120.5(4) |
| N(1)-C(1)-C(2) | 123.5(4) | N(1)-C(1)-H(1) | 118.3(4) |
| C(2)-C(1)-H(1) | 118.3(4) | N(1)-C(5)-C(4) | 123.7(4) |
| N(1)-C(5)-H(5) | 118.2(4) | C(4)-C(5)-H(5) | 118.2(4) |

| | | | |
|---|---|---|---|
| C(9)-C(10)-C(11) | 119.6(3) | C(9)-C(10)-H(10) | 120.2(4) |
| C(11)-C(10)-H(10) | 120.2(3) | O(4)-C(24)-C(23) | 116.8(4) |
| O(4)-C(24)-C(25) | 123.2(4) | C(23)-C(24)-C(25) | 119.9(4) |
| C(21)-C(26)-H(26) | 119.6(4) | C(21)-C(26)-C(25) | 120.9(4) |
| H(26)-C(26)-C(25) | 119.6(4) | C(24)-C(25)-C(26) | 120.1(4) |
| C(24)-C(25)-H(25) | 119.9(4) | C(26)-C(25)-H(25) | 120.0(4) |

In figurs 4 and 5 molecular struture of ligand $L_2$ and its unit cell are showen. As shown in figure 4 the molecular structure of this ligand is treedentate ($O_1$, $N_2$ and $N_3$ atoms) .

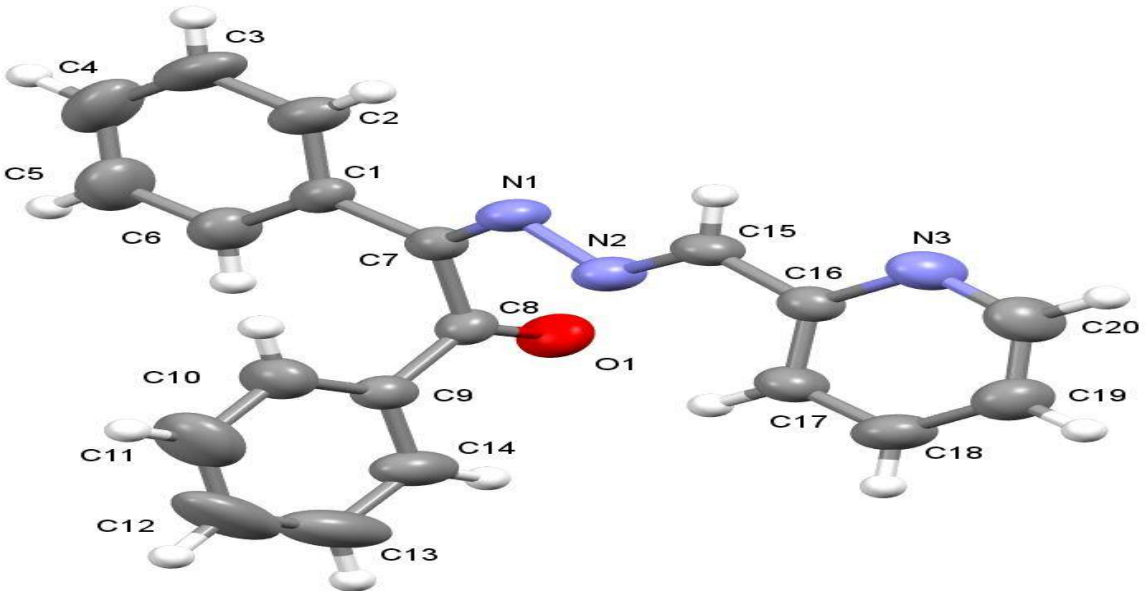


Figure4: Molecular structure of ligand ($L_2$=ABN-25)

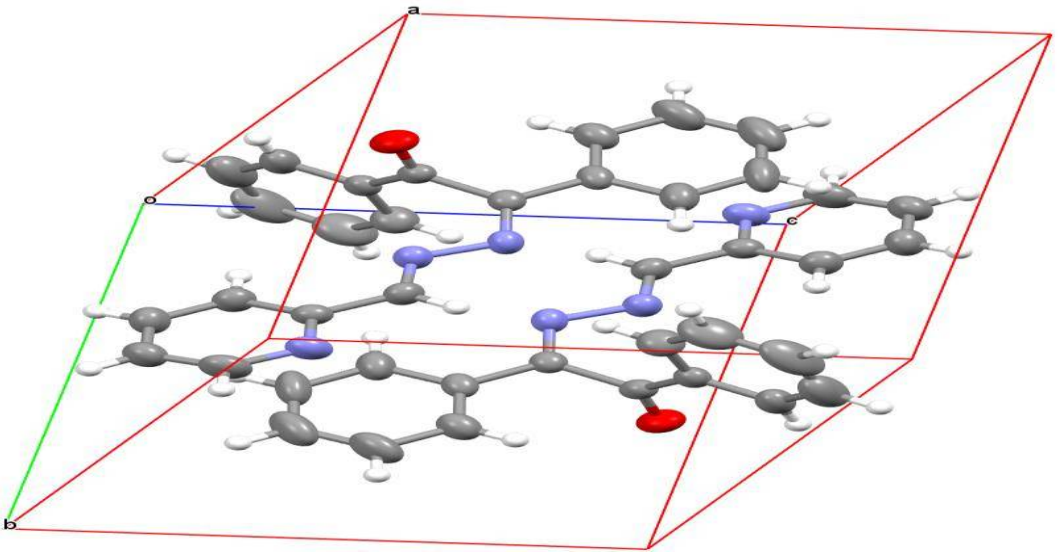


Figure5:Unit cell of ligand ($L_2$=ABN-25)

For ligand $L_2$ in below tables 4 and 5 bond angles and bond ditances. Complete listing of bond angles (degrees)(table 4), and the complete listing of bond ditances (table 5)

Table 4
Complete listing of bond angles (degrees). $L_2$=ABN-25

| | | | |
|---|---|---|---|
| C(16)-N(3)-C(20) | 116.3(3) | C(8)-C(9)-C(14) | 119.3(3) |
| C(8)-C(9)-C(10) | 120.5(3) | C(14)-C(9)-C(10) | 120.1(3) |
| O(1)-C(8)-C(9) | 123.3(2) | O(1)-C(8)-C(7) | 117.2(2) |
| C(9)-C(8)-C(7) | 119.4(2) | N(3)-C(16)-C(17) | 122.7(3) |
| N(3)-C(16)-C(15 | 115.4(2) | C(17)-C(16)-C(15) | 121.9(2) |
| N(1)-C(7)-C(8) | 120.4(2) | N(1)-C(7)-C(1) | 120.9(2) |
| C(8)-C(7)-C(1) | 118.6(2) | C(7)-C(1)-C(6) | 120.6(3) |
| C(7)-C(1)-C(2) | 120.7(3) | C(6)-C(1)-C(2) | 118.8(3) |
| C(16)-C(17)-H(17) | 120.5(3) | C(16)-C(17)-C(18) | 118.9(3) |
| H(17)-C(17)-C(18) | 120.5(3) | N(2)-C(15)-C(16) | 120.8(3) |
| N(2)-C(15)-H(15) | 119.6(3) | C(16)-C(15)-H(15) | 119.6(3) |
| C(9)-C(14)-H(14) | 120.5(3) | C(9)-C(14)-C(13) | 119.0(3) |
| H(14)-C(14)-C(13) | 120.5(3) | C(9)-C(10)-H(10) | 120.0(3) |
| C(9)-C(10)-C(11) | 119.9(3) | H(10)-C(10)-C(11) | 120.0(3) |
| C(1)-C(6)-H(6) | 119.6(3) | C(1)-C(6)-C(5) | 120.8(3) |
| H(6)-C(6)-C(5) | 119.6(3) | C(17)-C(18)-H(18) | 120.4(3) |
| C(17)-C(18)-C(19) | 119.2(3) | H(18)-C(18)-C(19) | 120.4(3) |
| C(18)-C(19)-H(19) | 120.9(3) | C(18)-C(19)-C(20) | 118.3(3) |
| H(19)-C(19)-C(20) | 120.9(3) | C(1)-C(2)-H(2) | 120.2(3) |
| C(1)-C(2)-C(3) | 119.7(3) | H(2)-C(2)-C(3) | 120.2(3) |
| N(3)-C(20)-C(19) | 124.6(3) | N(3)-C(20)-H(20) | 117.7(3) |

| | | | |
|---|---|---|---|
| C(19)-C(20)-H(20) | 117.7(3) | C(14)-C(13)-H(13) | 119.4(4) |
| C(14)-C(13)-C(12) | 121.2(4) | H(13)-C(13)-C(12) | 119.4(4) |
| C(2)-C(3)-H(3) | 119.6(4) | C(2)-C(3)-C(4) | 120.8(3) |
| H(3)-C(3)-C(4) | 119.6(4) | C(6)-C(5)-H(5) | 119.9(4) |
| C(6)-C(5)-C(4) | 120.1(4) | H(5)-C(5)-C(4) | 119.9(4) |
| C(3)-C(4)-C(5) | 119.7(4) | C(3)-C(4)-H(4) | 120.1(4) |
| C(5)-C(4)-H(4) | 120.1(5) | C(10)-C(11)-H(11) | 119.9(4) |
| C(10)-C(11)-C(12) | 120.1(4) | H(11)-C(11)-C(12) | 119.9(4) |
| C(13)-C(12)-C(11) | 119.5(4) | C(13)-C(12)-H(12) | 120.2(5) |
| C(11)-C(12)-H(12) | 120.2(5) | | |

Table 5
Complete listing of bond distances (Angstroms). $L_2$=ABN-25

| | | | |
|---|---|---|---|
| O(1) - C(8) | 1.221(3) | N(1) - C(7) | 1.286(3) |
| N(2) - C(15) | 1.257(3) | N(3) - C(16) | 1.340(3) |
| N(3) - C(20) | 1.334(4) | C(9) - C(8) | 1.473(4) |
| C(9) - C(14) | 1.383(4) | C(9) - C(10) | 1.373(4) |
| C(8) - C(7) | 1.518(3) | C(16) - C(17) | 1.380(3) |
| C(16) - C(15) | 1.459(3) | C(7) - C(1) | 1.472(3) |
| C(1) - C(6) | 1.384(4) | C(1) - C(2) | 1.384(4) |
| C(17) - H(17) | 0.930(3) | C(17) - C(18) | 1.371(4) |
| C(15) - H(15) | 0.930(3) | C(14) - H(14) | 0.930(3) |
| C(14) - C(13) | 1.367(5) | C(10) - H(10) | 0.930(3) |
| C(10) - C(11) | 1.374(5) | C(6) - H(6) | 0.930(3) |
| C(6) - C(5) | 1.378(5) | C(18) - H(18) | 0.930(3) |
| C(18) - C(19) | 1.363(4) | C(19) - H(19) | 0.930(3) |
| C(19) - C(20) | 1.363(4) | C(2) - H(2) | 0.930(3) |
| C(2) - C(3) | 1.383(4) | C(20) - H(20) | 0.930(3) |
| C(13) - H(13) | 0.930(4) | C(13) - C(12) | 1.368(7) |
| C(3) - H(3) | 0.930(3) | C(3) - C(4) | 1.372(7) |
| C(5) - H(5) | 0.930(4) | C(5) - C(4) | 1.363(5) |
| C(4) - H(4) | 0.930(4) | C(11) - H(11) | 0.930(5) |
| C(11) - C(12) | 1.372(6) | C(12) - H(12) | 0.930(4) |

## Conclusion:

With considering X-ray strutures of ligands, and melting point of them, and spectroscopic data, FT-IR, UV-Vis, $^1$HNMR, we could conclude that ligands acted as a ttree dentate ligand and coordination to metal via N imine and O benzohydrazide or 1,2-diphenyl and N pyridine atoms.

## References :

[1]. M.A.Naziri, 2004, Synthesise and Characterization of ..., Faculty of Chemistry, University of Tabriz.
[2]: B. Shaabani etal., Journal of Molecular Structure,1045,2013,55-61
[3].A.M.Stadler, J.harrowfield, inorganic Chemical Acta, 362,2009, 4298-4314