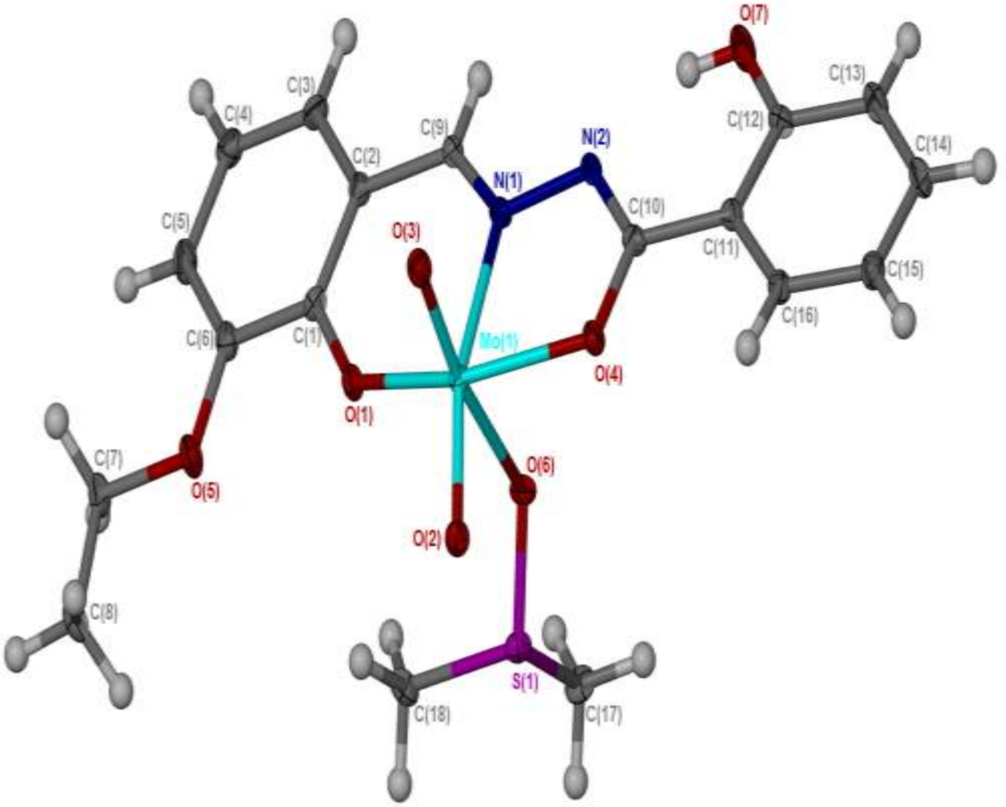

Figure 33: Ellipsoidal plot of C15 with 50% level of probability. The atomic coordinates were given in the Appendix on page 242.

The Mo – O (donor atom of solvent) bond length in the molecules are all found somewhat longer than the normal single bond length due to the consequence of the *trans* effect of M=O_t (where O_t is oxo-group *trans* to the Mo – $O_{solvent}$). This result reveals a rather weak attachment of the donor atom solvent to the MoO_2^{2+}. When the methanol coordinated MoO_2(VI) complexes are dissolved in stronger coordinating agents such as DMF, DMSO or HMPA, methanol molecule is tend to be displaced by these solvent molecules.

The equatorial bases formed by O1, O2, O4 and N1 in the complexes are not coplanar. The Mo atom in molecular structures of **C6** and **C13** are found to have shifted 0.2010 Å and 0.2233 Å, respectively, out from the basal plane towards the apical oxo-oxygen atom O3 while the other structures show a displacement of the metal atom towards the donor atom of the solvent, O6.

In Schiff base metal complexes, the environment at the coordination center can be modified by attaching different substituent to the ligands, which provide a useful range of steric and electronic properties essential for the fine-tuning of structure. Mononuclear dioxomolybdenum(VI) complexes containing Schiff base ligands can be assembled into various supramolecular architecture by means of intermolecular non covalent forces.

In the molecular structure of **C8** (Fig.34), intramolecular O-H…N hydrogen bonding (OH…N, 2.602(4) Å) in the Schiff base ligand helps to stabilize the overall structure. In addition, the presence of O-H….O hydrogen bonding (O7H…O2, 2.826(4)Å and O7H…O6, 3.069(4)Å) links the molecules into a polymeric chain parallel to the *ab* crystallographic plane (table 29). The unusual long Mo1 – O6 bond length (2.337Å) and the O6 – Mo1 – O2 angle (176 .18°) is the consequences of the hydrogen bond interaction of the

C8 molecules. In the crystal structure of **C13** (Fig. 35), the presence of a methanol molecule which is hydrogen bonded to the imidazole nitrogen (N-H…O, 2.864(6) Å) resulted in a layer structure propagated along the *bc* crystallographic plane. The π-π stacking contacts between the imidazole rings *Cg1-Cg1*' (symmetry code: 1-x, 1-y, 1-z where *Cg1* is the centroid of the imidazole ring) may further reinforce the crystal packing, with centroid-centroid average distance of 3.813(2) Å (table 30). An intra-molecular hydrogen bonding (O7-H7…N2, 2.5859 (19) Å) and other weak intermolecular interactions (O9-H9…O3, 3.217(2) Å; C18-H18…O3, 3.238 (2)Å) were found in **C15** (table 31; fig.36). On the other hand, **C6, C7** and **C12** exist as discrete molecule with no evidence of any hydrogen bonding interaction.

Table 29. Hydrogen bonds in **C8** [Å and ^{o}].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...N(2)	0.82	1.89	2.601(4)	144.7
O(5)-H(5A)...O(3)#1	0.82	2.55	3.075(4)	123.5
O(7)-H(7A)...O(2)#2	0.82	2.20	2.826(4)	133.0
O(7)-H(7A)...O(6)#2	0.82	2.30	3.069(4)	155.6

Symmetry transformations used to generate equivalent atoms:
#1: -x+1,-y+2,-z+1 #2: x+1,y,z

Table 30: Hydrogen bonds in **C13** [Å and ^{o}]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...O(7)	0.86	2.02	2.862(5)	165.4

Symmetry code: #1 -x+1,-y+2,-z+1

Table 31: Hydrogen bonds in **C15** [Å and ^{o}]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O7-H7….N2	0.82	1.87	2.5859 (19)	145
C9-H9...O3#	0.93	2.54	3.217 (2)	130

Symmetry code: #1 -x+1,-y+2,-z+1

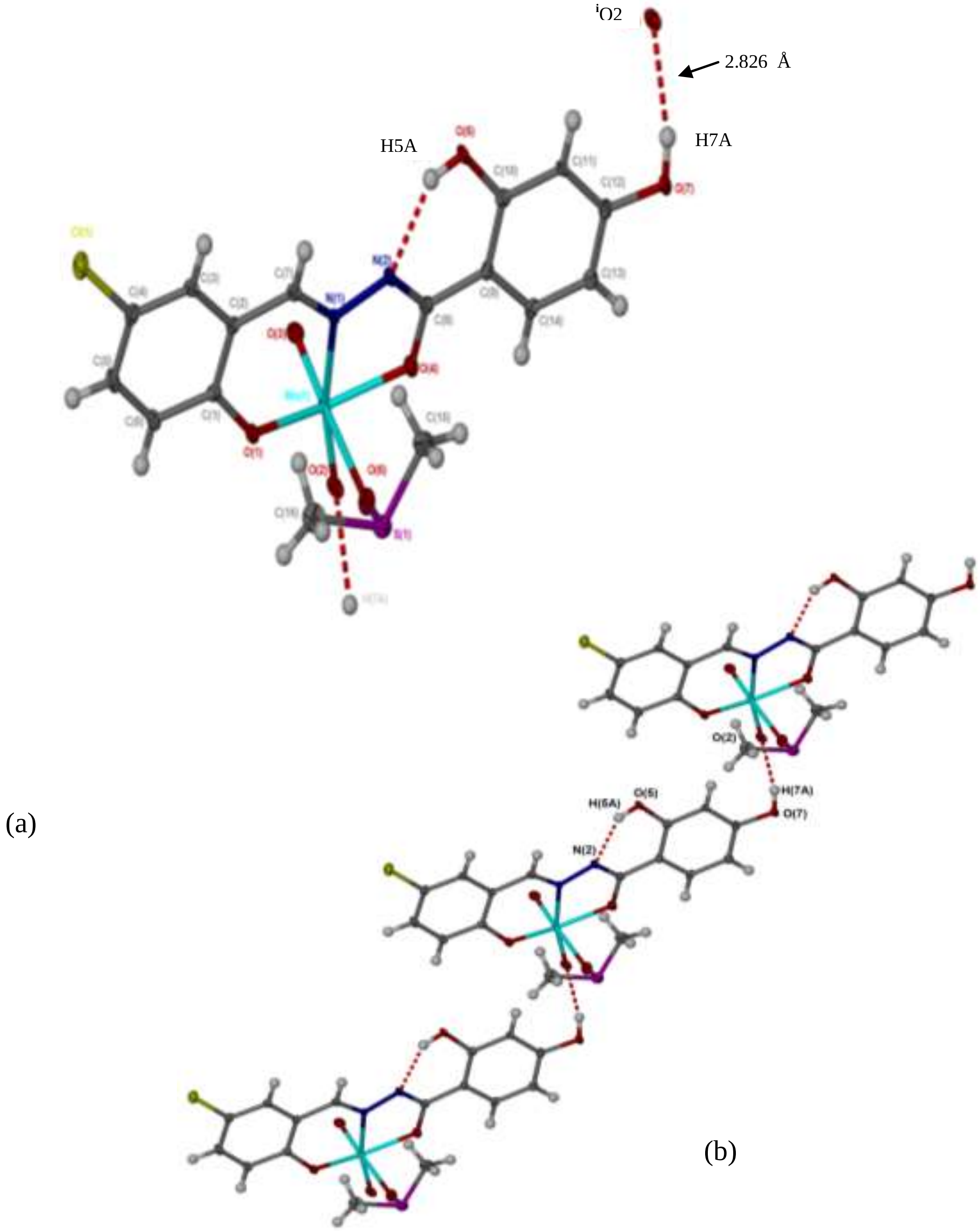

Figure 34(a) & (b): Ellipsoidal plot of C8 with 50% level of probability. Hydrogen bond represented by dotted line. Symmetry code (i) : x+1,y,z

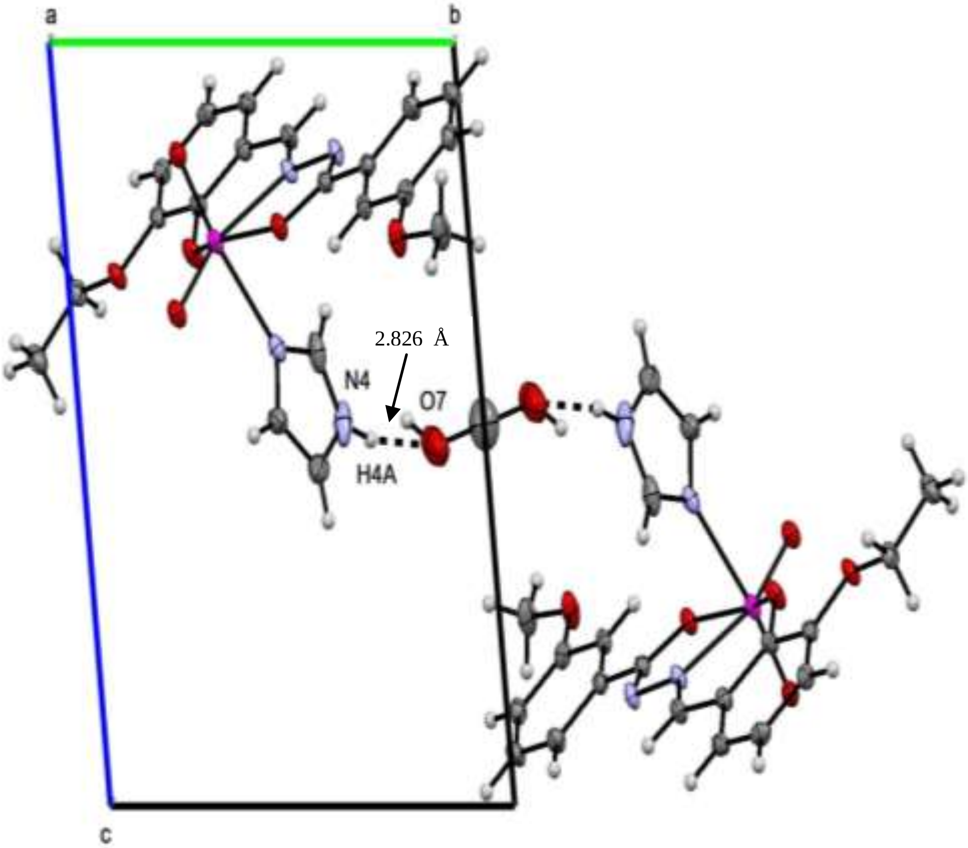

Figure 35: Crystal packing of C13, with the atom labelling scheme. Hydrogen bond represented by dotted line.

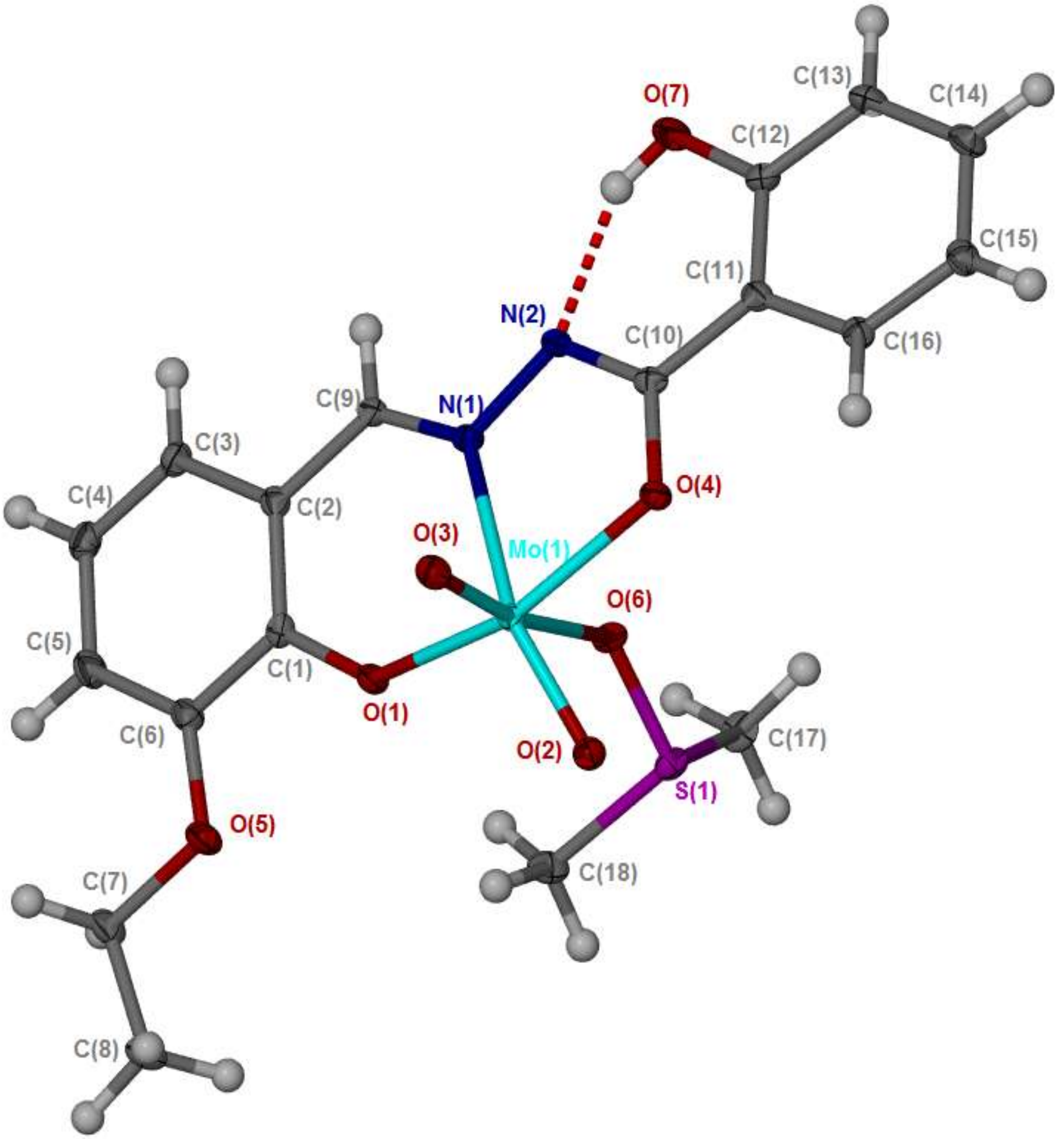

Figure 36: Ellipsoidal plot of C15 with 50% level of probability. Intramolecular hydrogen bond represented by dotted line.

3.7.4 Crystallographic description of the Complexes C16

In the present study, by using a Schiff base that possesses substituent groups leads to a solvent-coordinated derivative in which 4,4'-bipyridine interacts indirectly, through the solvent molecule, in an outer-sphere coordination mode. In the co-crystal, $MoO_2(CH_3OH)(C_{14}H_9ClN_2O_4).C_{10}H_8N_2$ **C16,** the deprotonated Schiff base *O,N,O*'-chelates to the Mo(VI) atom, the three atoms involved in chelation comprising the *meridonal* sites of the octahedron surrounding the methanol-coordinated metal center (Figs. 37&38). The solvent molecule forms an O–H···N hydrogen bond to a N atom of the 4,4'-bipyridine molecule; the hydroxyl group forms an O–H···N hydrogen bond to the other N atom of another molecule, the two hydrogen bonds leading to the formation of a helical chain that runs along the *b*-axis of the monoclinic unit cell (table 32).

Table 32. Hydrogen bonds in **C16** [Å and ^{o}].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O2-H2...N1	1 0.84 (1)	1.85 (3)	2.600 (4)	147 (6)
O3-H3…N3	0.84 (1)	1.92 (2)	2.741 (5)	166 (6)
O7-H7... N4#	0.84 (1)	1.84 (1)	2.679 (4)	175 (6)

Symmetry code#: -x+1/2, y+1/2, -z+1/2

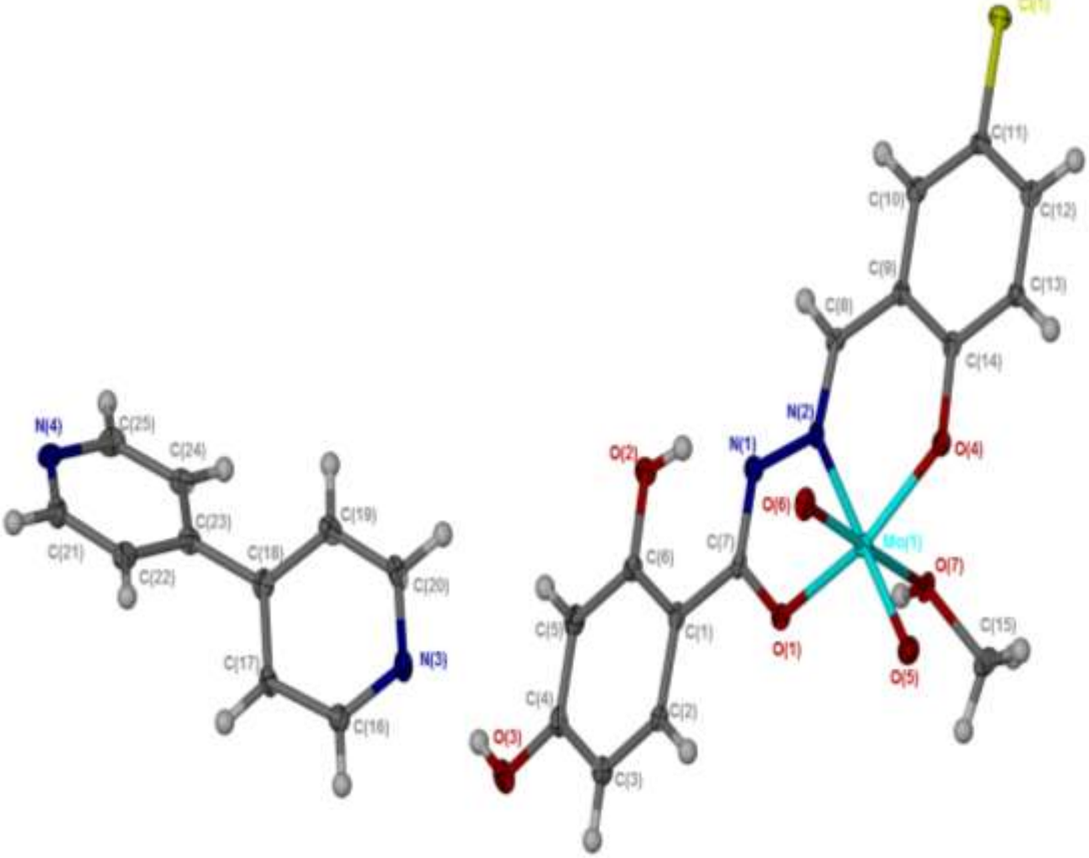

Figure 37: Ellipsoidal plot of C16 with 50% level of probability. The atomic coordinates were given in the Appendix on page 243.

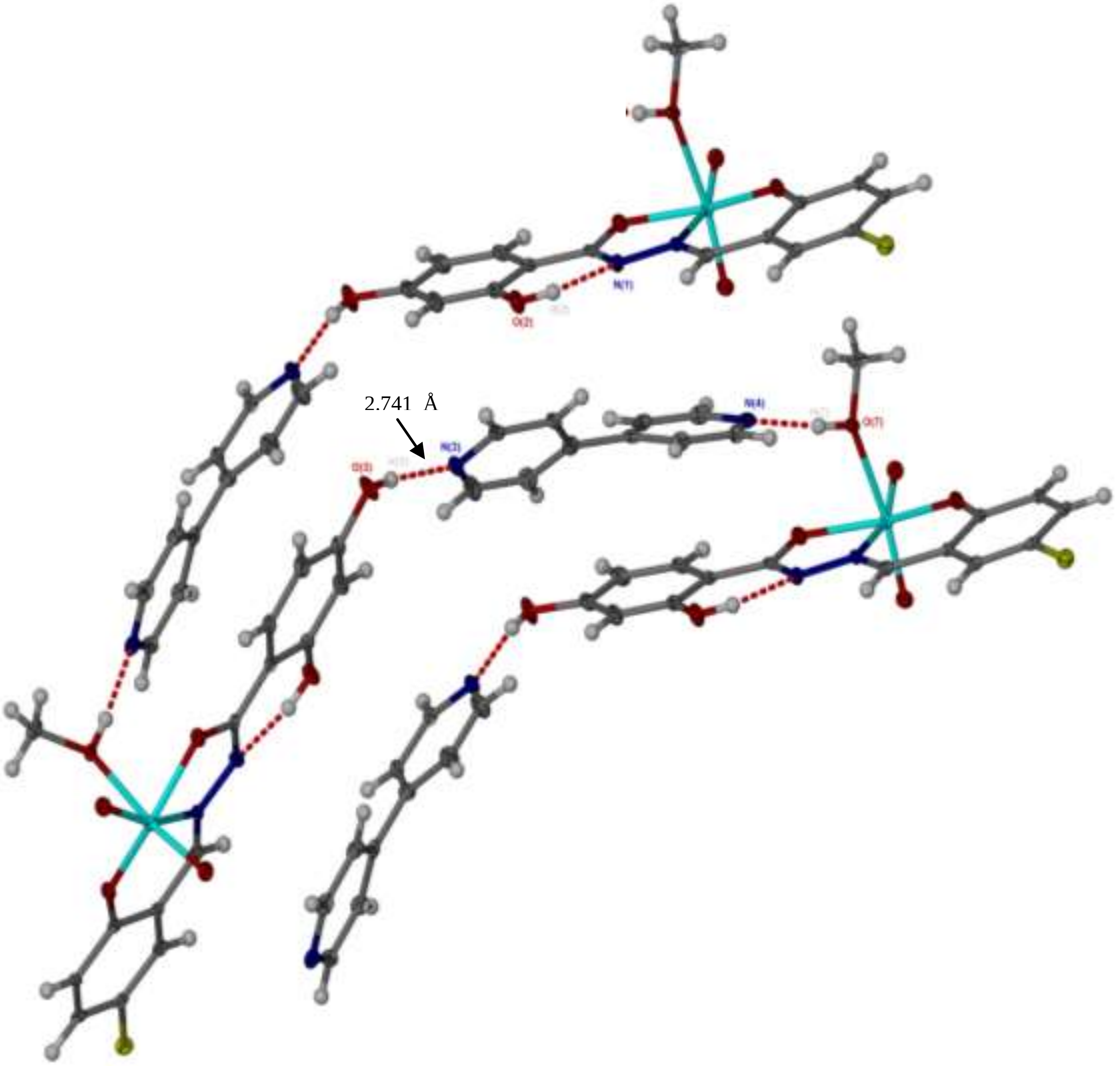

Figure 38: Hydrogen bond generated helical chains along *b* axes of the monoclinic unit cell of C16.