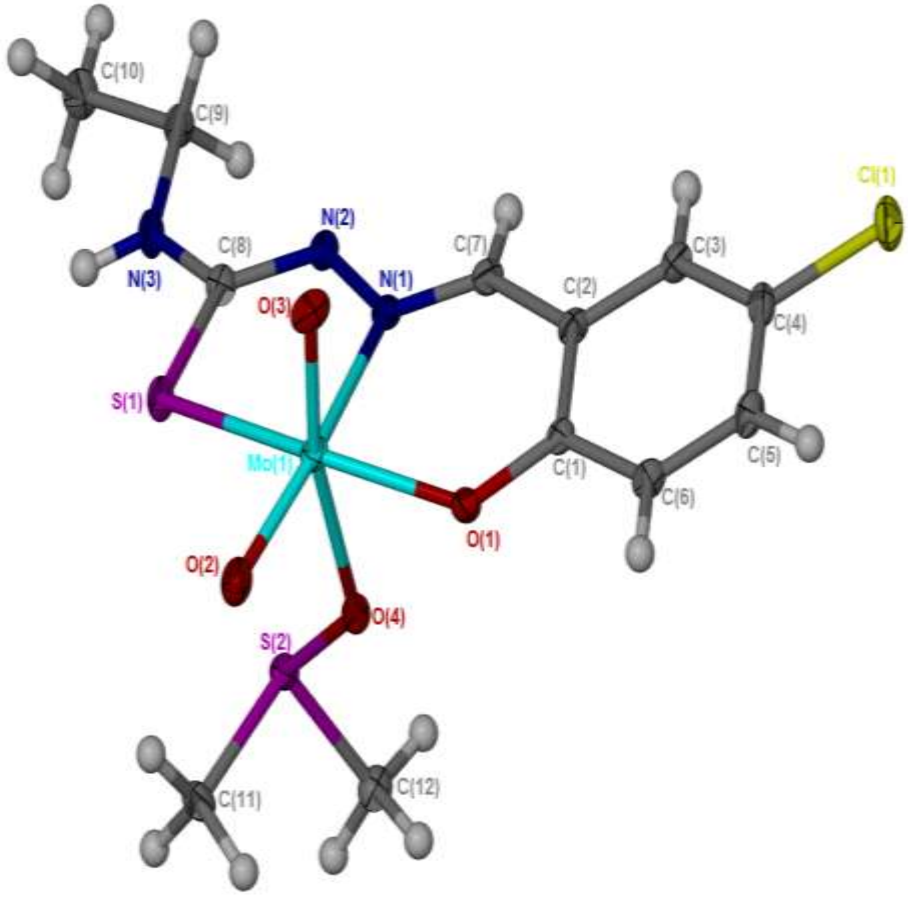

Figure 19: Ellipsoidal plot of C2 with 50% of level of probability. The atomic coordinates were given in the Appendix on page 231.

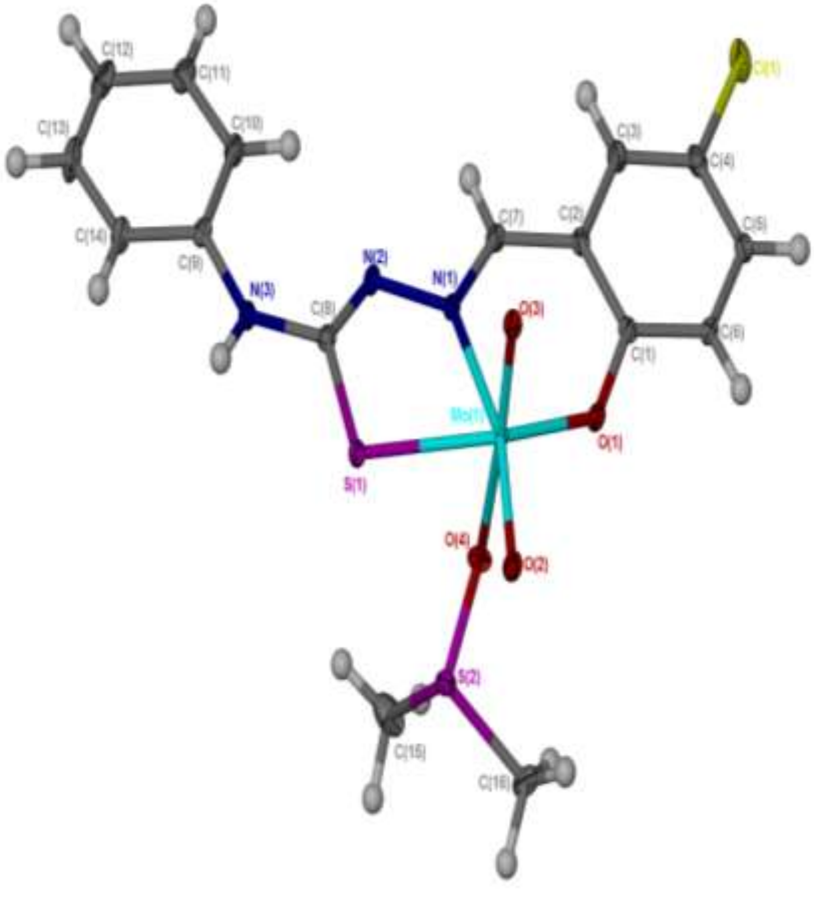

Figure 20: Ellipsoidal plot of C3 with 50% of level of probability. The atomic coordinates were given in the Appendix on page 232.

The Mo=O bond lengths and the O=M=O angles have values which are in the expected range for *cis*-dioxomolybdenum(VI) complexes [74-77]. The bond distance between the Mo and the oxygen atom from DMSO [2.312(2)Å (**C1**), 2.2628(19)Å (**C2**), 2.3366(15)Å (**C3**)] suggested that DMSO binds firmly to the MoO_2^{2+} moiety.

The equatorial bases formed by S1, O2, O1 and N1 in the complexes are non planar. The Mo atom of **C1** and **C2** are shifted 0.2507 Å and 0.2359 Å, respectively out from the basal plane towards the solvent oxygen donor atom, O4, while the Mo atom of **C3** show a 0.2466 Å displacement towards the apical oxo-oxygen atom, O3.

In the crystal structures of **C1** and **C3** (Figs.21&22), the molecules are arranged in polymeric networks that are parallel to the *bc* and *ab* crystallographic plane, respectively as shown in table 27 and 28. The **C1** molecules are held more firmly by two hydrogen bonds *via* N(3)-H(2)...N(2) [3.000Å] and N(3)-H(1)...O(4) [2.897Å], whereas in the case of **C3** the molecules are merely connected by a rather weak N(3)-H(3)...O(4) hydrogen bond as indicated by its bond length, d(D...A) of 3.23 Å. As a result, the molecules forms infinite chain that runs along the *a*-axis. The hydrogen bond length of **C1** molecules is shorter than that of **C3** reveal rather stronger intermolecular interaction governing the alignment of the molecules in **C1** packing. This is confirmed by the TGA study, which exhibited easy decomposition of **C3** molecules on controlled heating.

Table 27. Hydrogen bonds in **C1**

D-H...A	d(D-H) Å	d(H...A) Å	d(D...A) Å	<(DHA) (^{o})
N(3)-H(2)...N(2)#	0.77	2.25	3.000(4)	163.5
N(3)-H(1)...O(4)##	0.83(4)	2.08(4)	2.897(3)	167(4)

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

Table 28. Hydrogen bonds in **C3**

D-H...A	d(D-H) Å	d(H...A) Å	d(D...A) Å	<(DHA) (^{o})
N(3)-H(3)...O(4)	0.88	2.41	3.231(2)	154.9

Symmetry code: x-1, y, z

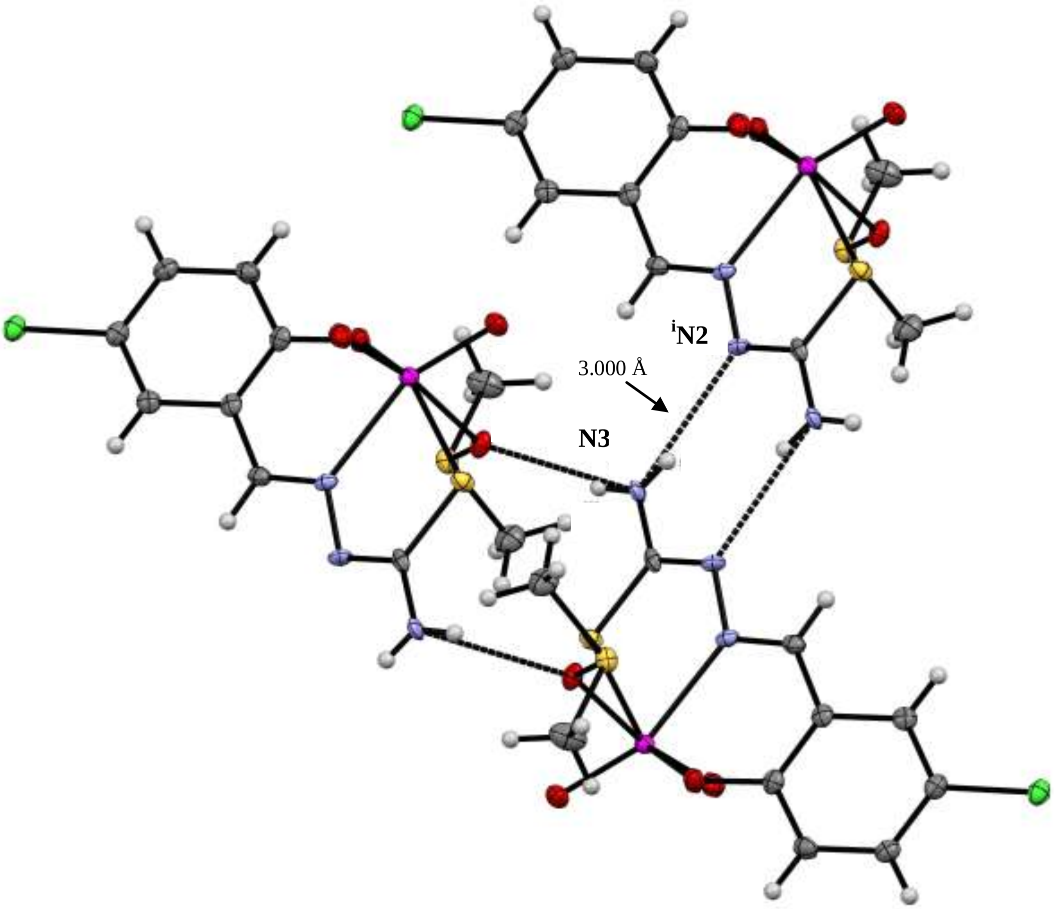

Figure 21: Arrangement of C1 molecules showing hydrogen bond interaction in dotted line. Symmetry code (i) : x+2, -y, -z+1

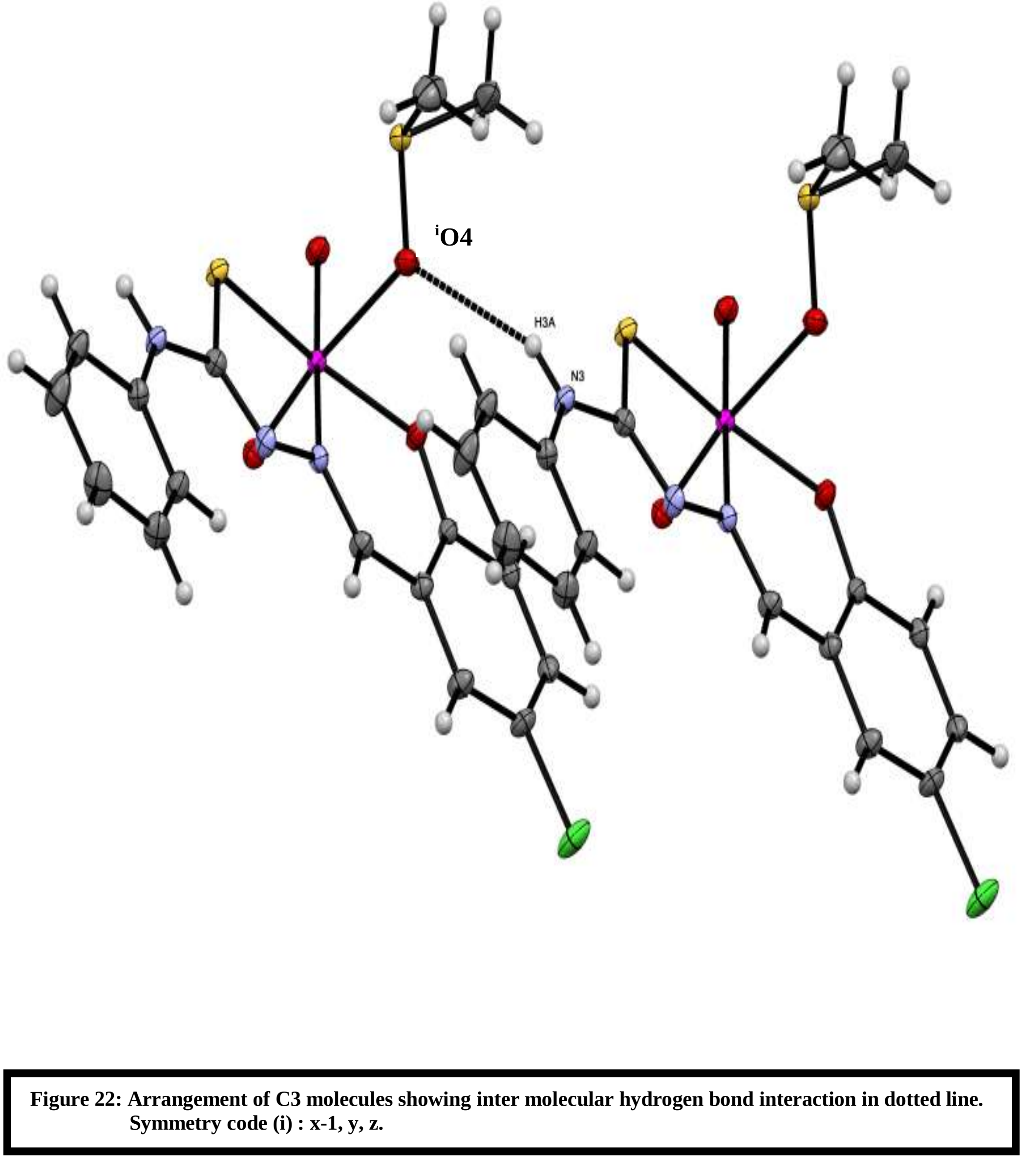

Figure 22: Arrangement of C3 molecules showing inter molecular hydrogen bond interaction in dotted line. Symmetry code (i) : x-1, y, z.

3.7.3 Crystallographic description of the Mononuclear Dioxomolybdenum(VI) Complexes with –ONO donor ligands system

The molecular structures (Figs. 23-33) show that in all the complexes, the Schiff base ligands behaved as tridentate ligands, and reacted with the dioxomolybdenum anion to form six coordinated molybdenum(VI) structures. As shown in the figures, the imine nitrogen, one of the phenoxyl oxygen and the hydroxyl oxygen from the enolized carbonyl group are involved in the coordination with molybdenum atom, forming six- and five-member chelate rings around the *cis* MoO_2 centre. In all of the complexes, the Mo = O bond lengths which ranges from 1.693(2) – 1.721(2)Å and the O = Mo = O bond angles which lies between 104.23(2) – 105.40(2)^o are similar to those reported for other MoO_2 complexes. The bond distance between Mo and phenolate oxygen, Mo and deprotonated nitrogen, and Mo between enolate oxygen are also close to those found in other ONO tridentate Schiff base molybdenum(VI) complexes.

The C-O bond distance in all the complexes exhibit values between 1.309 -1.326 Å, which is nearer to C-O single bond than to a C-O double bond distance. This shows that the ligand coordinates to the MoO_2 core in the deprotonated enolate form [78-80]. On the other hand, the C=N bond length of *ca.* 1.28 Å in all the complexes confirms its significant double bond character. The values of N-N and C-N bond distance of *ca.*1.40 and 1.29 Å, respectively, which are greater than the value of a double bond and less than the value of a single bond, indicating the significant delocalization of π electron density over the ligands. Because of the short N-N bond length, the ligands act mostly as tridentate ligands.

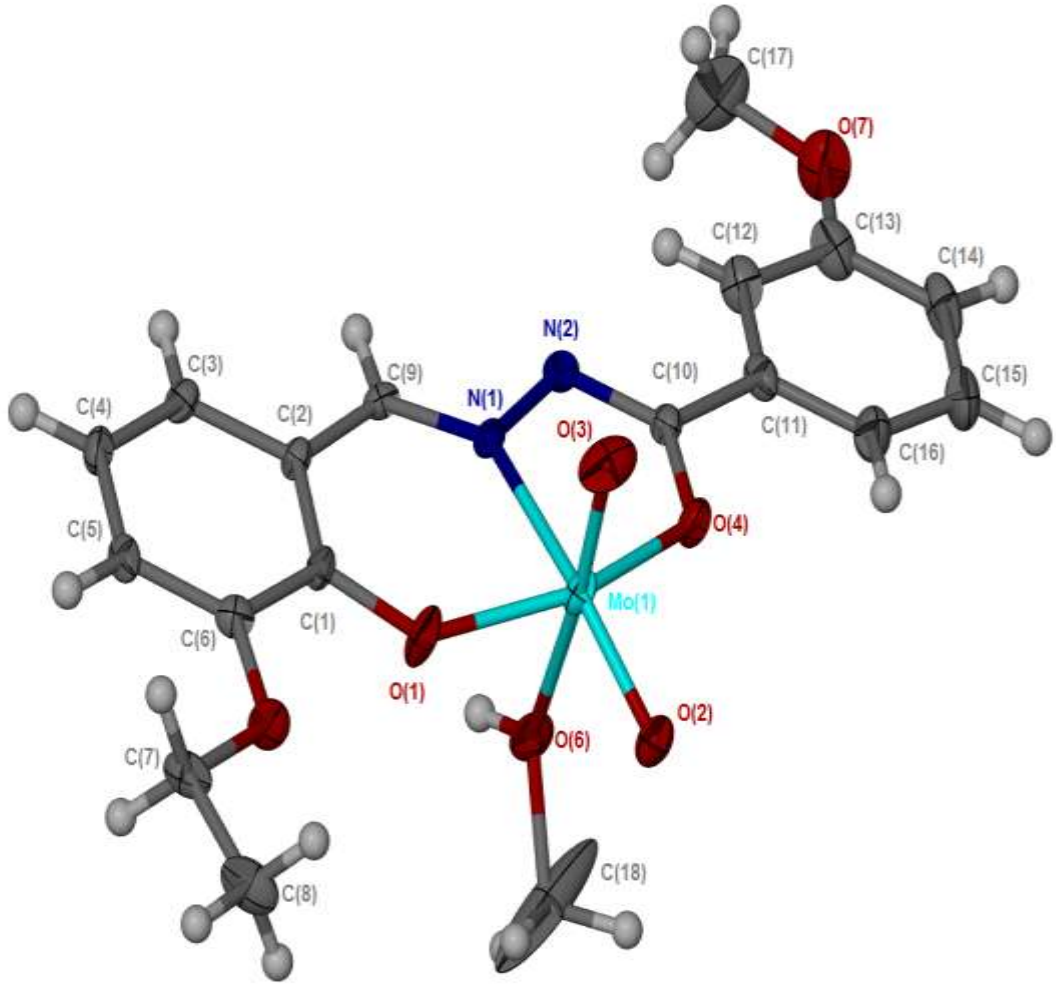

Figure 23: Ellipsoidal plot of C4 with 50% level of probability. The atomic coordinates were given in the Appendix on page 233.

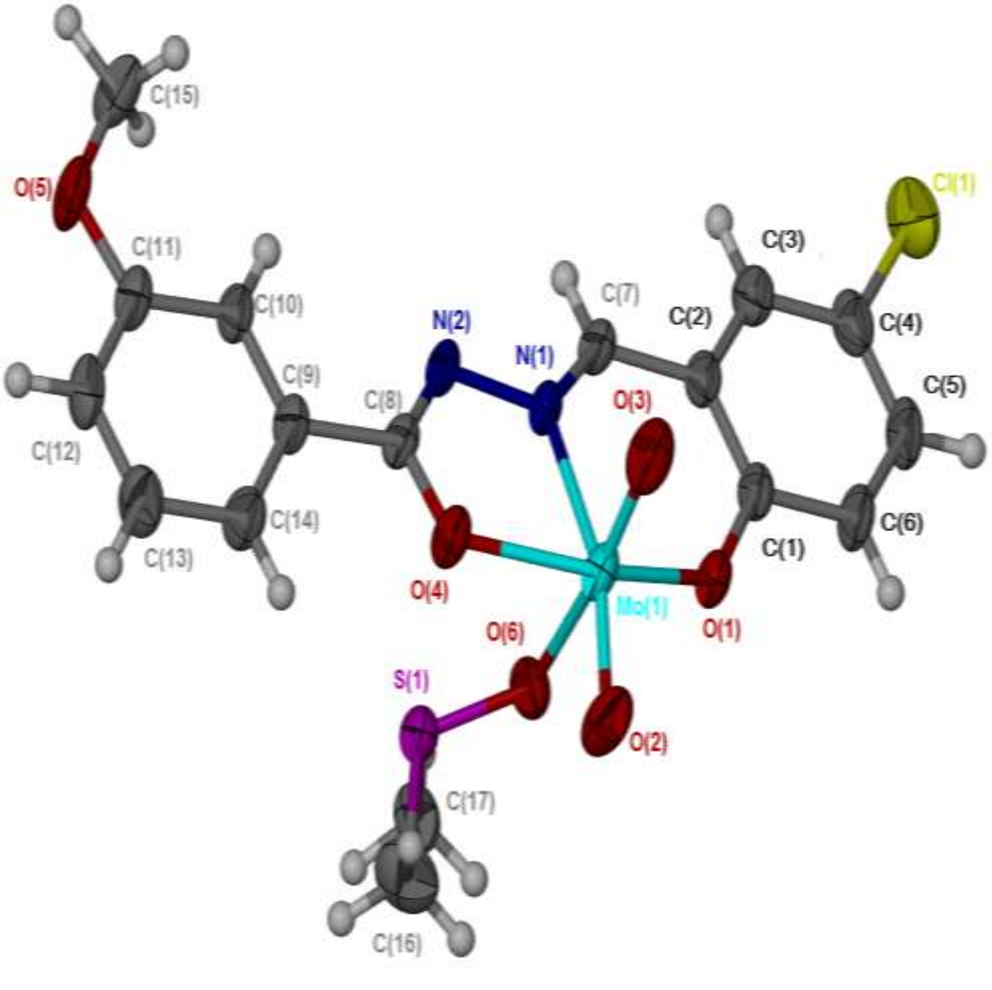

Figure 24: Ellipsoidal plot of C6 with 50% level of probability. The atomic coordinates were given in the Appendix on page 234.

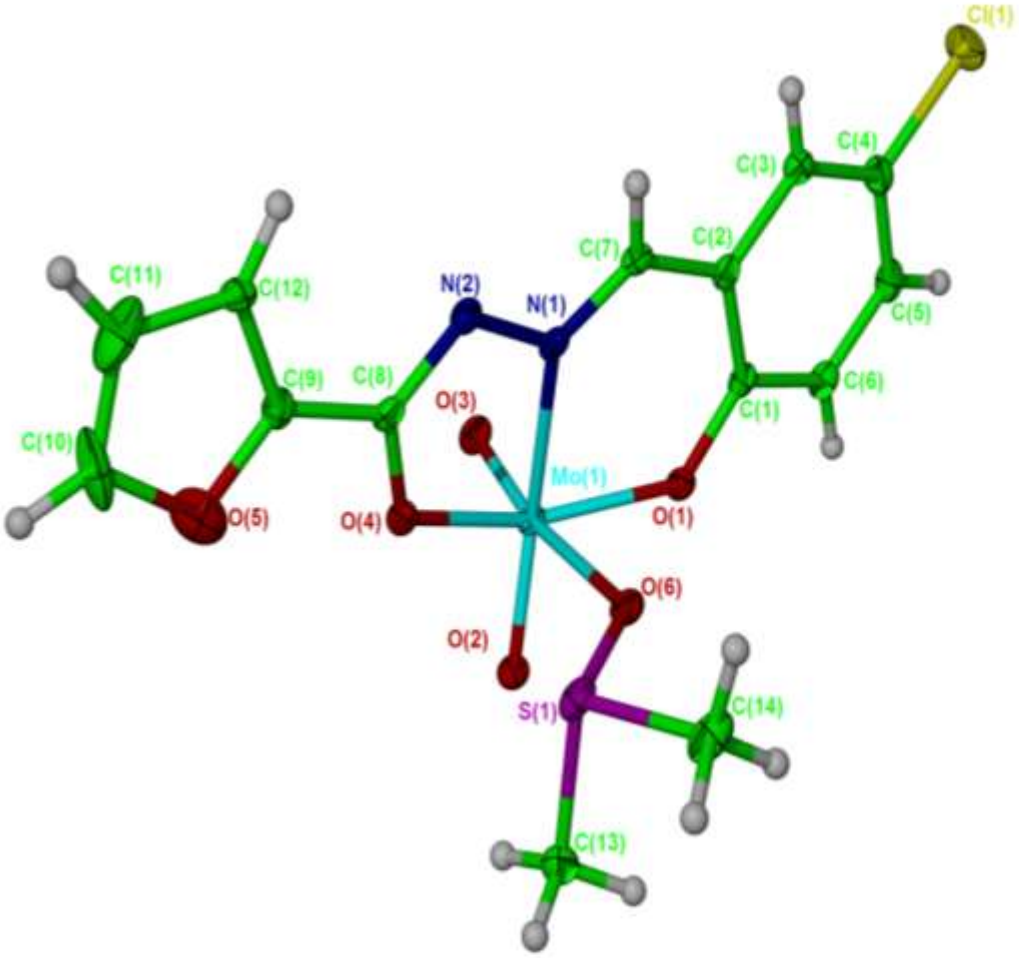

Figure 25: Ellipsoidal plot of C7 with 50% level of probability. The atomic coordinates were given in the Appendix on page 235

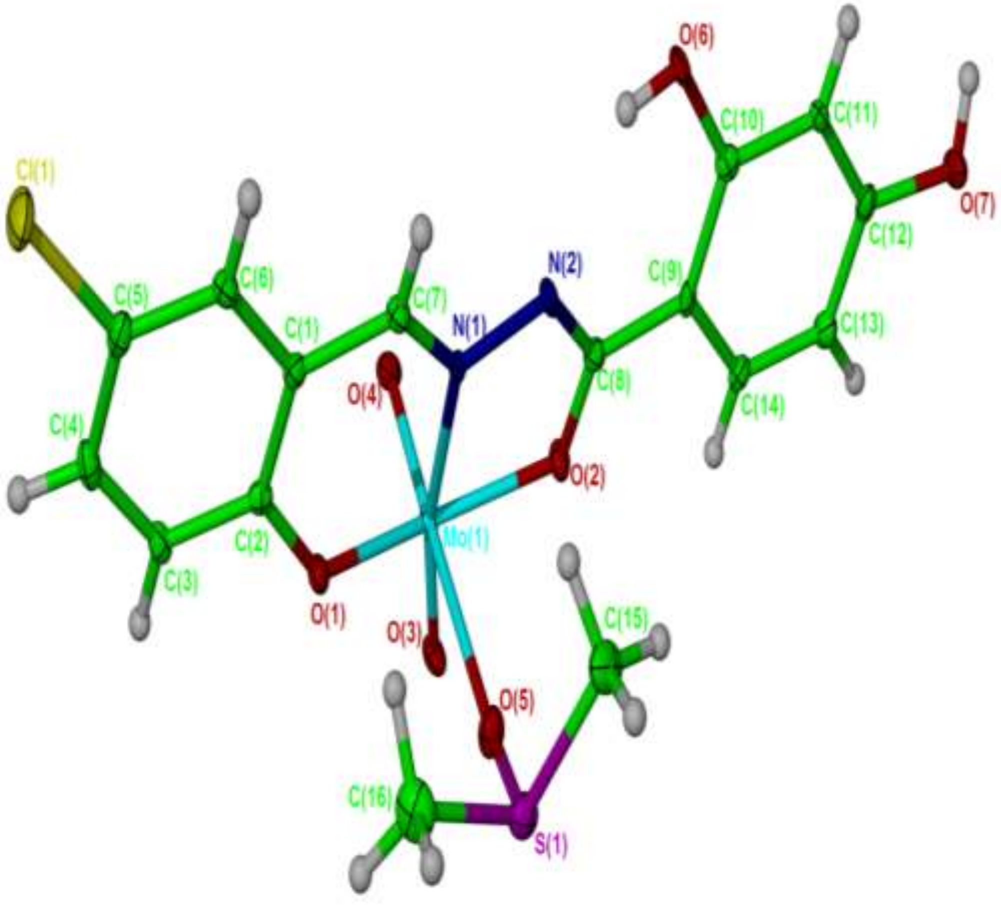

Figure 26: Ellipsoidal plot of C8 with 50% level of probability. The atomic coordinates were given in the Appendix on page 236