Quantitative crystal structure analysis of Complex: tris((1-((E)-o-tolyldiazenyl)naphthalen-2-yl)oxy)cobalt
.

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1- INTRDUCTION.

The development of metal complexes based on azo compounds has grown considerably in recent years. This is due to the diversity of the fields of application offered by these compounds. One of the most important areas where coordination compounds contain azo compounds is used in textile chemistry.

They are mainly based on chromium, copper, cobalt, nickel….etc. They are used for coloring cotton, wool, polyamide, leather. Indeed, these materials have the advantage of being able to combine the properties from the organic compound and the inorganic compound, while giving hope for a synergy between these two properties.

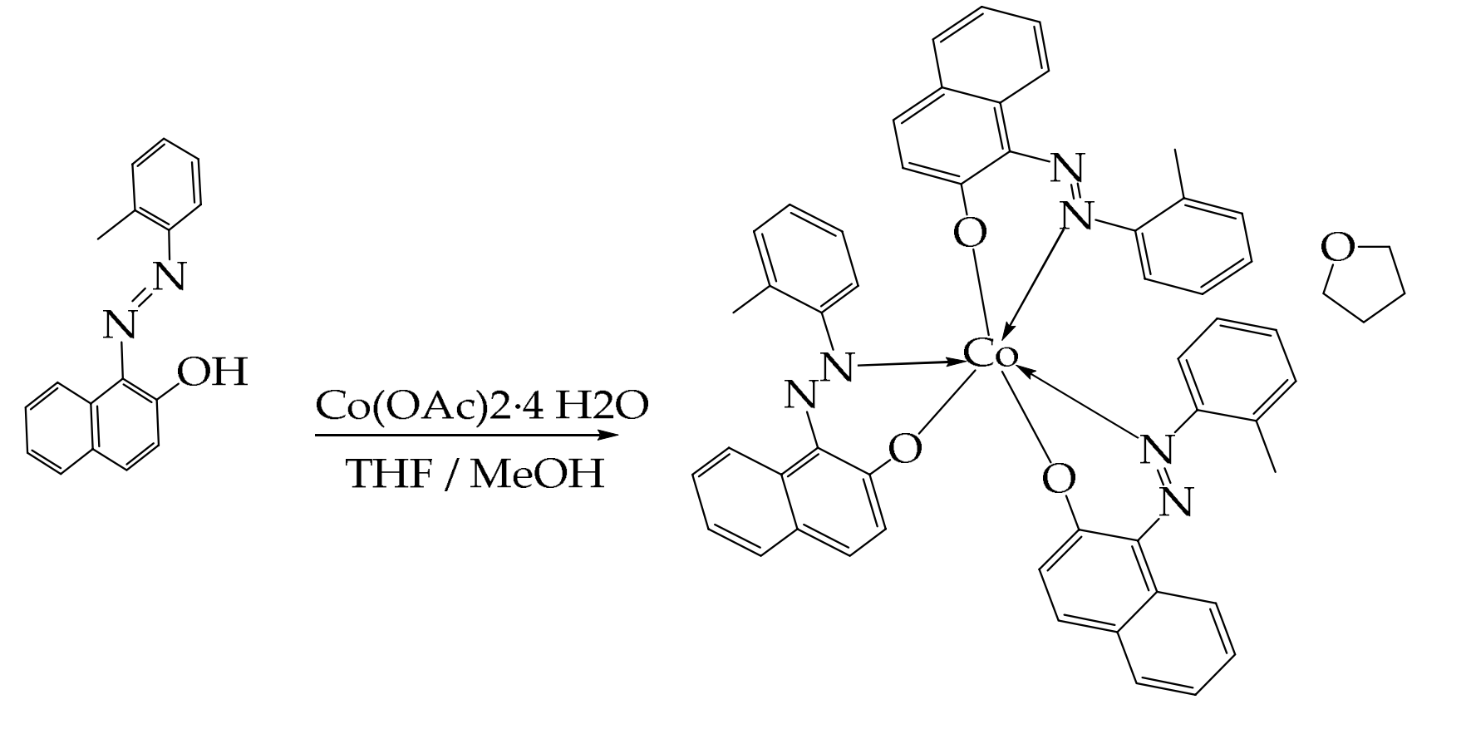
Metal complex dyes exhibit excellent unison dyeing and penetration characteristics and utilize the ability to cover surface irregularities. They have good light fastness and wash fastness properties even for dark shades.

We develop in the following the synthesis of an organic-inorganic hybrid material based on an azo compound using cobalt acetate. In which it will be treated by a detailed study of the crystal structure by X-ray diffraction, the spectroscopic methods; infrared and proton nuclear magnetic resonance

2- EXPERIMENTAL.

Our monoatomic Cobalt (II) complex was prepared by adding 0.003 mol of the ligand 1- (o-tolyldiazenyl) naphthalen-2-ol to 0.001mol of Co (OAc) 2.4H2O in a mixture of THF / MeOH (10/10 ml). The reaction mixture remained under stirring for 12 h at room temperature. Volatiles were removed in vacuo.

Brown crystals were obtained after a period of a few days by slow evaporation of the solution at room temperature. These could be isolated under an optical microscope for further X-ray analysis. The reaction scheme for the different stages of the synthesis of our complex is shown 1 below:



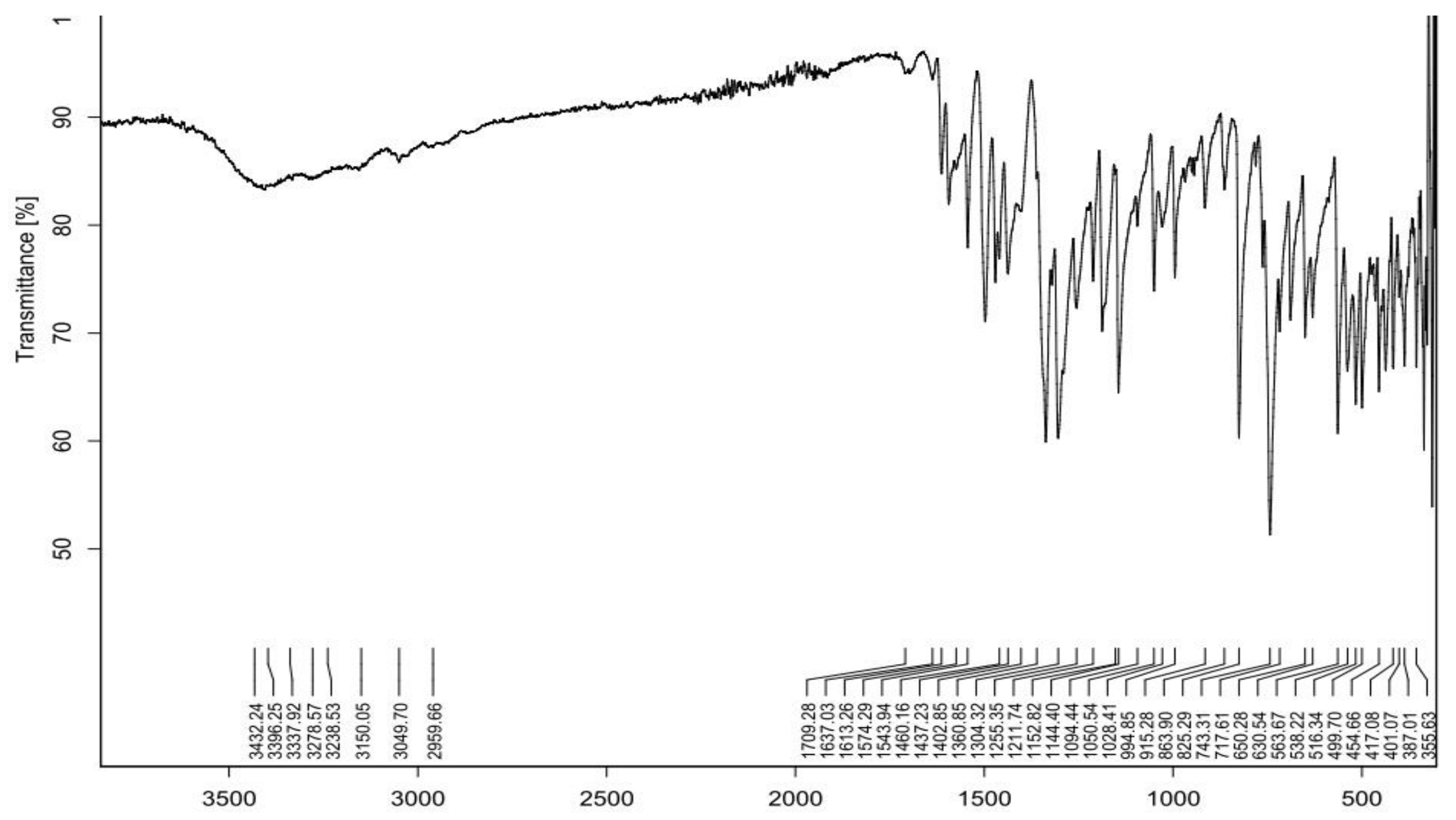
Scheme 1 : Synthesis of complex

3- RESULTS AND DISCUSSION.

The functional groups have been identified using infrared spectroscopy and proton nuclear magnetic resonance.

3-1- Infrared spectra

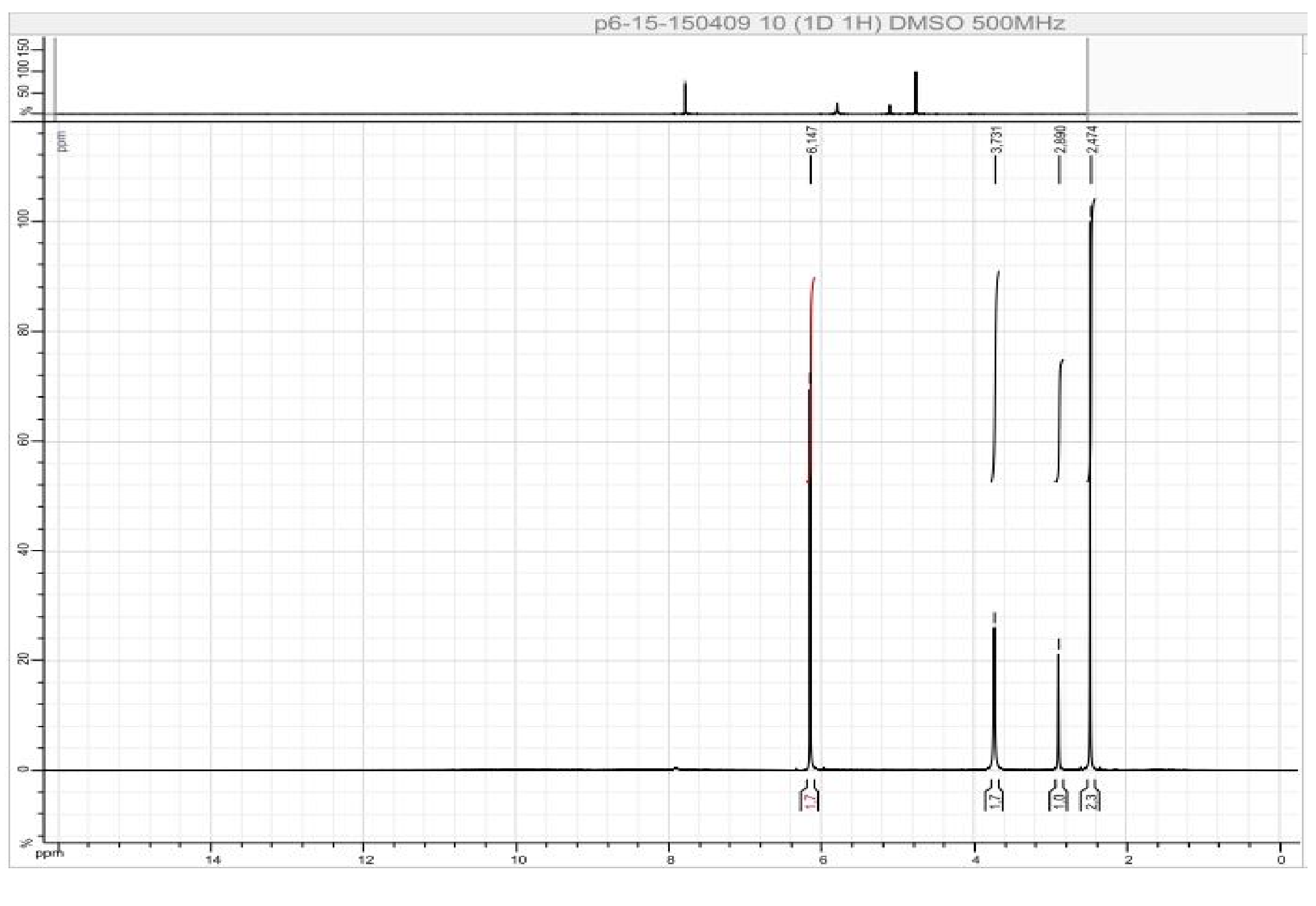
The infrared spectrum of this compound show a band located at 1360 cm-1 which is attributed to the N = N function, an absorption around 1144 cm-1 is due to the band of the CN bond, a band appearing at 1211 cm-1 is attributed to the mode of vibration of the CO bond (aromatic). in the spectra is the usual modes of aromatic ring vibrations and these reveal small shifts in the complex than in the free ligand, which is due to the expected electronic structure changes upon coordination. The proposed assignments are based on previous results and pertinent bibliography. while bands have a frequencies 630 cm-1 and 563 cm-1 indicating coordination through the oxygen atom and the nitrogen atom.



IR spectrum

3-2- NMR spectra

In the 1 H NMR spectrum the multiplets at 6 - 8 ppm corresponds to the aromatic protons. The disappearance of the signal at around 16 ppm belongs to the labile H of the hydroxyl (O-H……N) ligand, thus confirming the formation of the Co-O coordination, in place of H-O.



^{1}H NMR spectrum

3-3- X-ray diffraction

The crystal of the compound tris((1-((E)-o-tolyldiazenyl)naphthalen-2-yl)oxy)cobalt, was obtained in a test tube from a ethanol saturated solution through the slow evaporation of the solvent; the crystals were dried and separated for analysis of X-ray diffraction.

The crystalline data for this compound can be seen in Table 1 . The complex crystallizes in a monoclinic system a = 11.114 (3) Å b = 180.690 (5) Å c = 22.229 (6) Å, β = 110.015 °, presenting space group P21 / c with Z equal to 4 repeat units per unit cell, which comprises a volume of 4338.8 Å3. Figure 1 represents the repeat unit of the complex formed.

Table 1: Crystal data of Cobalt complex

Chemical formula	$C_{55}H_{47}CoN_6O_4$
weight (g/mol)	914.54
Unit cell dimensions	a = 11.1142 (3) Å b = 18.6906 (5) Å
	β = 110.015 (2)° c = 22.2292(6)Å
Crystal system	Monoclinique
Space group	$P2_1/c$
V (Å^3)	4338.8 (2)
Z	4
D_{cal} (g/cm^3)	1.4
Absorption coefficient (mm^{-}1)	0.45
F(000)	1912
$R[F^2>2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 4.0091P]$
$wR(F^2) = 0.126$	avec $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} = 0.008$
7669 No. of measured, independent	$\Delta\rho_{max} = 0.67$ e Å^{-3}
5980 observed reflections [I > 2σ(I)]	$\Delta\rho_{min} = -0.52$ e Å^{-3}

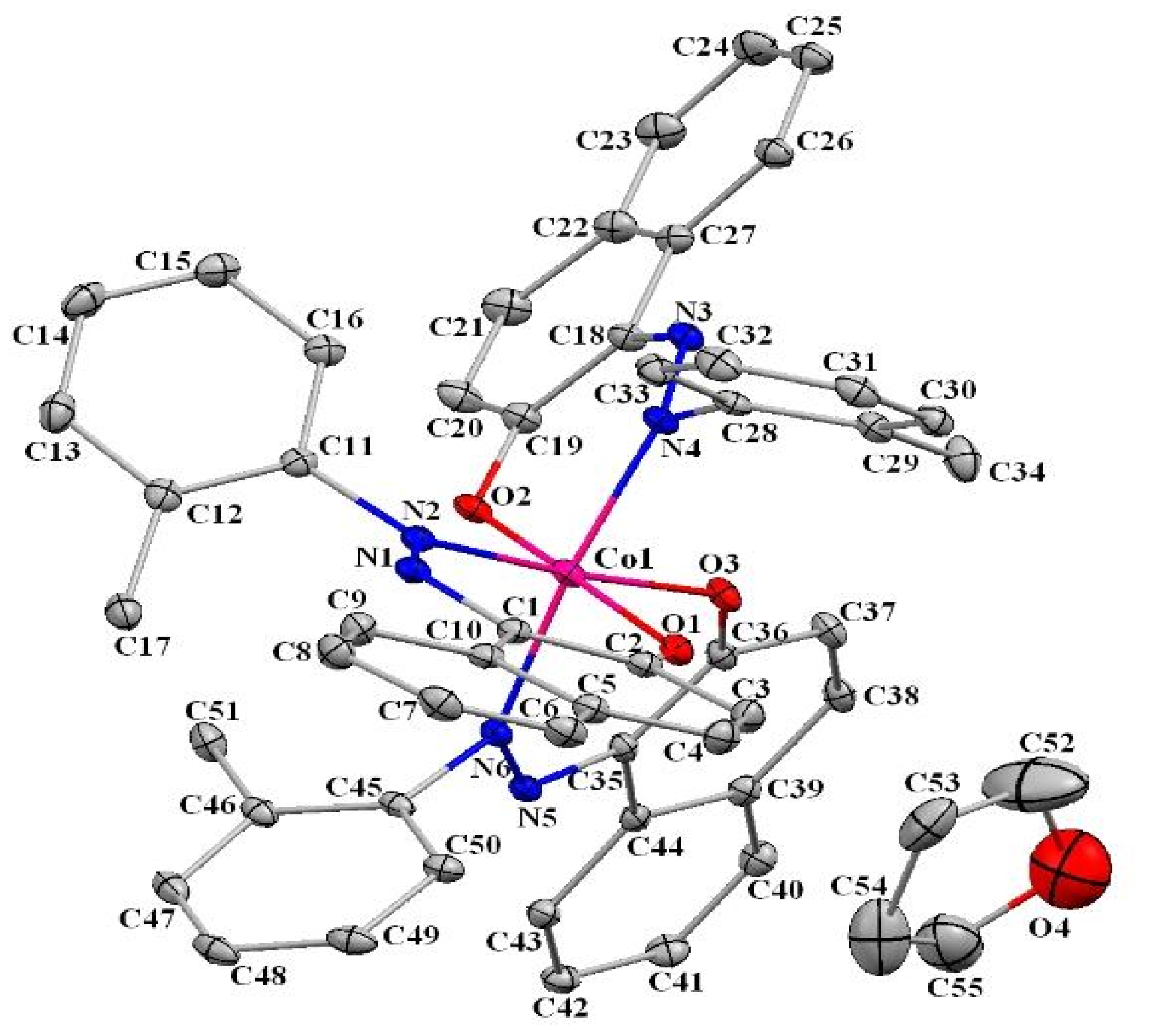


Figure 1.The asymmetric unit of Cobalt (II) complex (H atoms have been omitted for clarity).

For this compound the building block was formed through the coordination between three azo dyes and the cobalt ion; the metallic site appears coordinated in an octahedral geometry slightly distorted, with the bond angles between the O1– Co - O3, O2 - Co - O3, N2 - Co – N4 and N2 - Co - N6 atoms presenting values of 86.39 °, 87.38 °, 92.71 °and 95.75 ° respectively. However, we notice that the angles (O - Co - N) have values varying between 82.32 ° - 93.77°.

The structure described here of the ML3X3 type presents three bidentate ligands and it exists in the form isomer (mer) in which the two of the three identical atoms (O1; O2; O3 or N2; N4; N6) are Trans and therefore these three Identical atoms are on the same plane passing through the metallic center.

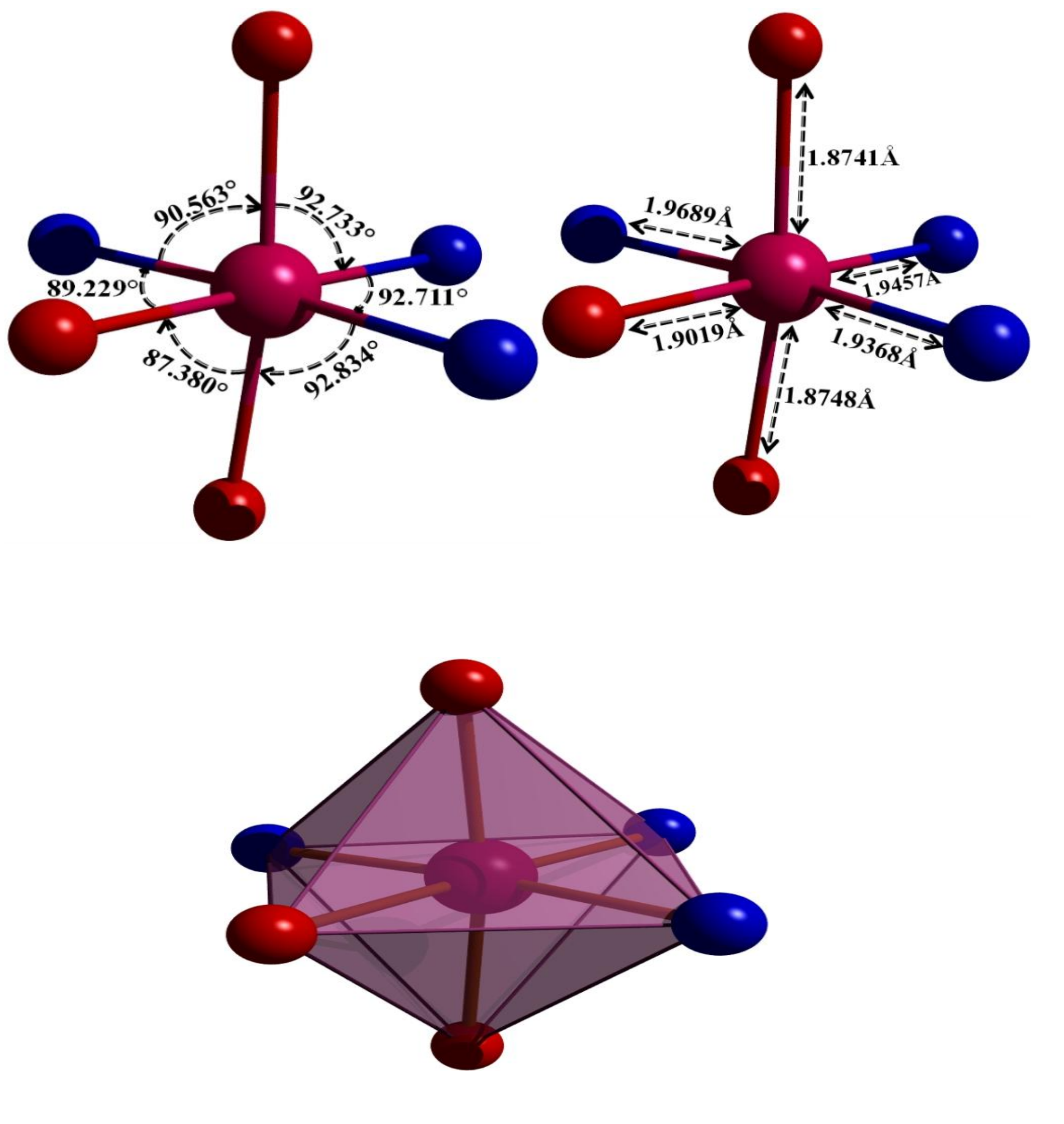
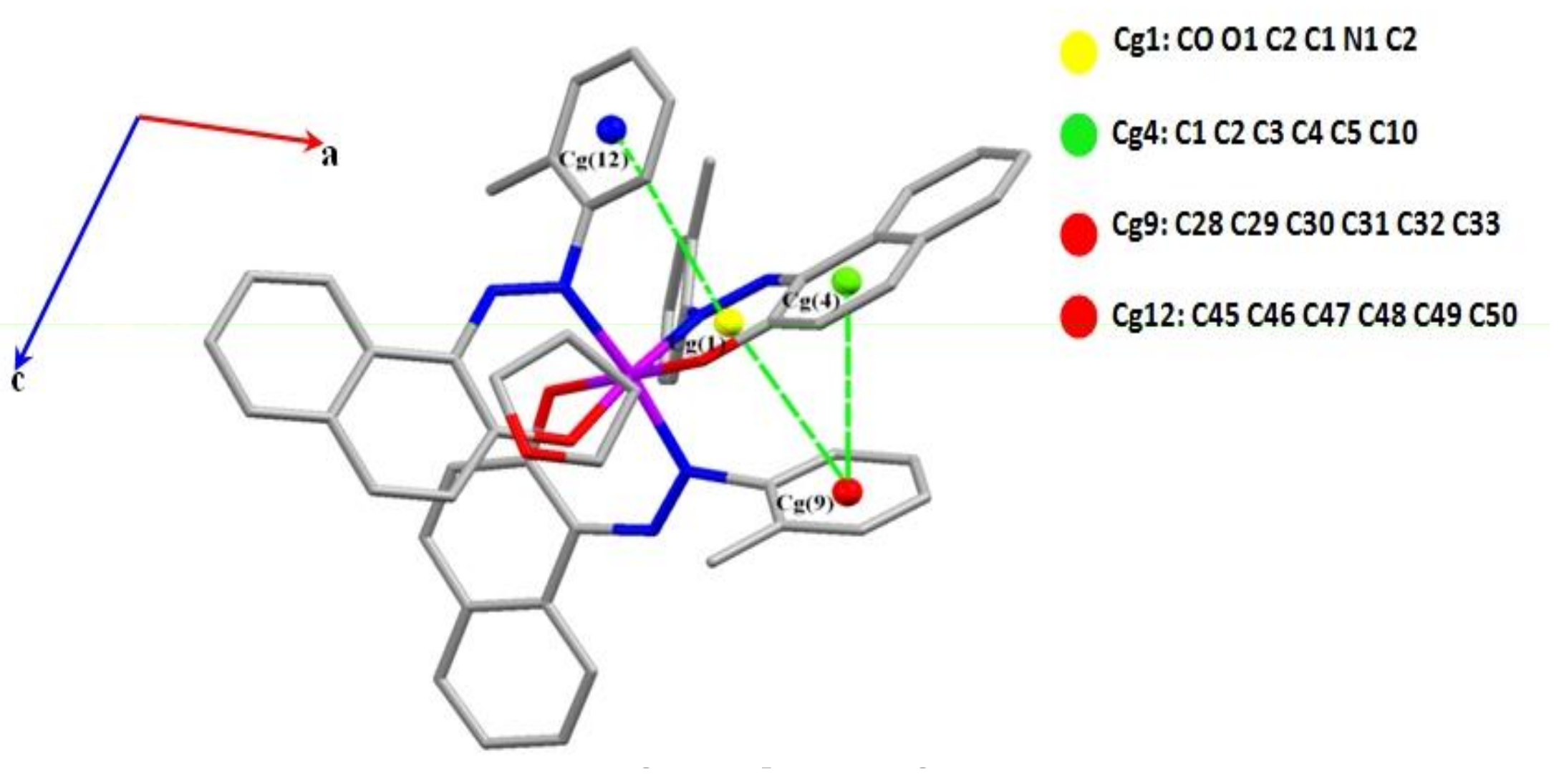


Figure 2. Environment of the cobalt atom

The solid state arrangement displays supramolecular interactions of the p- stacking type between the rings of the benzene group(Cg9,Cg12) and the center of gravity Cg1 which represents the center of the ring (Co O1 C2 C1 N1 N2). The distance between the two centroids from the naphthol groups (opposite rings) is 3.534 Å and 3.834 Å. Further interaction is observed between the Cg9 center of gravity of the benzene ring, with the Cg4 center of gravity of the naphthalene ring with a distance of 3.759Å, these interactions play an important role in the structural stability of the complex (Figure 3).



The C-H…..π interactions generated by our complex are essentially of four types; the first is an intramolecular type interaction between C17-H17B and the center of gravity Cg12 with a distance [C17-H17B…….Cg12 = 2.69 Å] and the second is that observed between aromatic CH (C14-H14, C15-H15) and the centers of gravity (Cg12, Cg9) of the benzene ring with distances [C14-H14…..Cg12 = 2.94 Å, and C15-H15……..Cg9 = 2.90 Å], the third observed between aromatic CH (C30-H30, C32-H32) and the centers of gravity (Cg11, Cg8) of the naphthalene ring with distances [C30-H30…...Cg11= 2.96 Å, and C32-H32……Cg8 = 2.94Å]. However the latter is linked the THF molecule with the complex, this distance interaction [C55-H55B…..Cg10 = 2.79 Å] (Figure 4). All of the C-H ……π interactions are reported in Table 2.

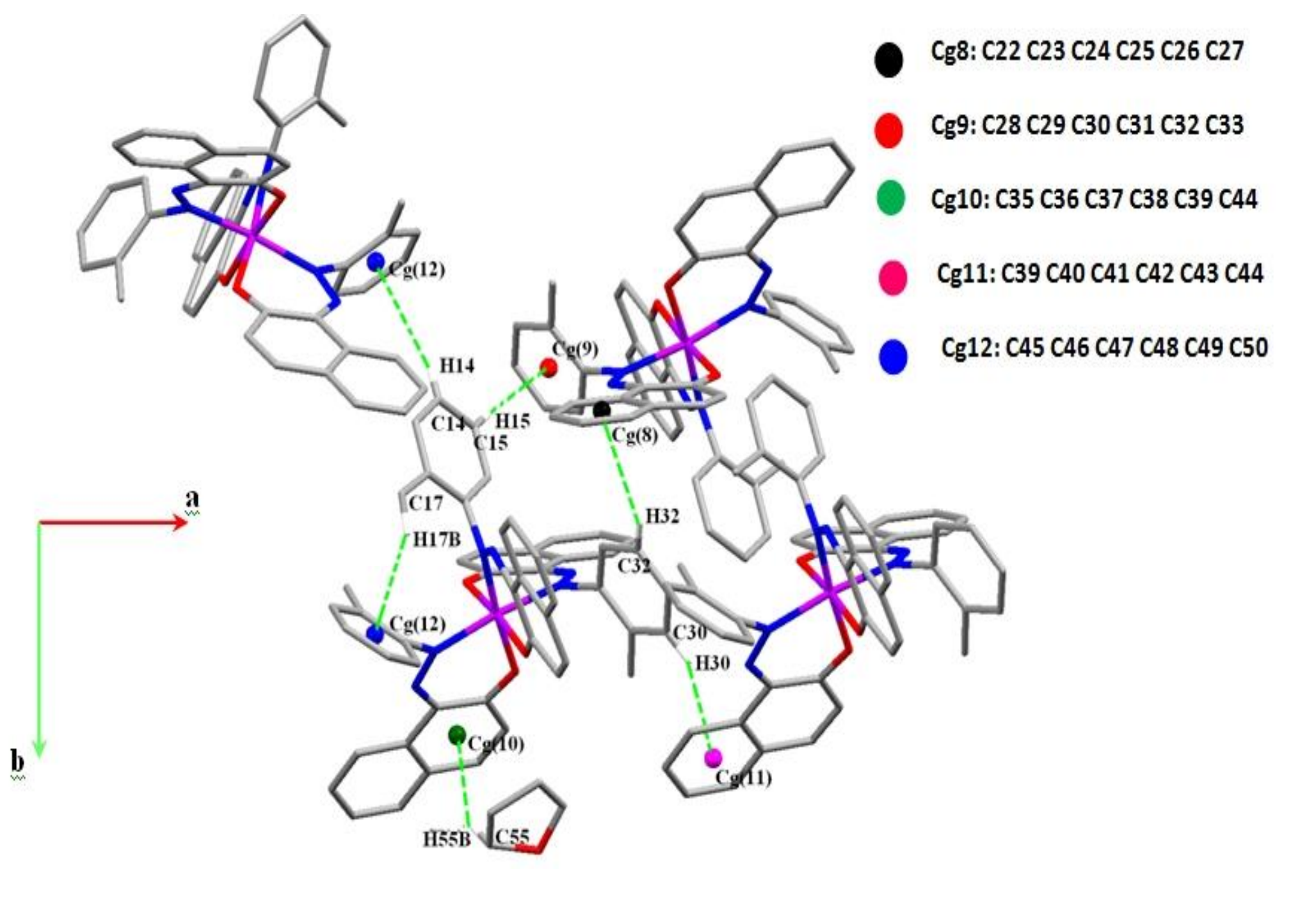


Figure 4. C-H·····π interactions

Table 2. interactions C-H….π

X--H(I)	CgI	H….Cg(Å)	X….Cg(Å)	X-H….Cg(°)
C17-H17B	Cg12i	2.694	3.562	151
C14-H14	Cg12ii	2.938	3.803	155
C15-H15	Cg9iii	**2.903**	**3.828**	**173**
C30-H30	Cg11iv	2.964	3.736	141
C32-H32	Cg8iii	2.941	3.602	129
C50-H50B	Cg10i	2.788	3.669	151

Symmetry codes: (i) : X,Y,Z, (ii) : -X,-1/2+Y,1/2- (iii) : Z1-X,1-Y,1-Z (iv) : 1+X,Y,Z.
Cg8 : The centroids of the benzene ring (C22…C27).
Cg9 : The centroids of the benzene ring (C28…C33).
Cg10 : The centroids of the benzene ring (C35…C39-C44).
Cg11: The centroids of the benzene ring (C39…C44).
Cg12 : The centroids of the benzene ring (C45…C50).

These distances suggest an arrangement, which is maintained united by p-stacking and CH/p supramolecular interactions, which are observed between the centroids of the naphthol groups and CH/p, being notably important for the packaging of this crystalline system.

4- CONCLUSIONS.

A coordination compound derived from 1- (o-tolyldiazenyl) naphthalen-2-ol were synthetized with cobalt ion present octahedron geometry. X-ray diffraction and spectroscopic methods: IR, 1H-NMR among other techniques experimental and theoretical were used for structural elucidation of this compound. Supramolecular interactions based on p-stacking type between the two centroids from benzen rings were observed at 3.534 Å ,3.834 Å and 3.759 Å; another important supramolecular interaction was observed between the CH from the phenyl group and the centroid of the benzen group, with the average distance of 3.600 Å.

References

1- Benaouida M. A., Benosmane A., Bouguerria H., Bouaoud S., & Merazig H., Acta Cryst. E69, M405. (2013).
2- Benosmane A., Benaouida M. A., Mili A., Bouchoul A. and Merazig H., Acta Cryst. (2015).
3- Mili A., Chetioui S., Rouag D.-A., Djukic J.-P. and Bailly C. IUCRDATA .1, X160691.(2016).
4- Ferreira G.R., de Oliveira L.F.C., Journal of Molecular Structure 1146 50e56 (2017).
5- Al-Adilee K.,. Kyhoiesh H.A.K, Preparation and identification of some metal complexes with new heterocyclic azo dye ligand 2-[2-(1-hydroxy-4-chloro phenyl) azo]-imidazole and their spectral and thermal studies, J. Mol. Struct.1137 160e178 (2017).
6- Gup R., Giziroglu E., Kırkan B., Synthesis and spectroscopic properties of new azo-dyes and azo-metal complexes derived from barbituric acid and amino-quinoline, Dyes Pigments 73 40e46 (2007).