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SUPPORTING INFORMATION

Synthesis and crystal structure determination of a mononuclear cobalt(II) complex derived from 4–(pyridin–4–ylmethoxy)–benzoic acid: Evaluation of the DNA/protein interaction and photo–induced pBR322 DNA cleavage

Sartaj Tabassum[a*] Ruchi Singh[b], Mehvash Zaki[a], Musheer Ahmad[c] Mohd. Afzal[a]

[a]*Department of Chemistry,Aligarh Muslim University, Aligarh, UP–202002, India.*
[b]*Department of Chemistry, Indian Institute of Technology Kanpur (UP) 202002 India.*
[c]*Department of Applied Chemistry, Aligarh Muslim University, Aligarh, UP–202002, India.*
** Corresponding author:*
Aligarh Muslim University, Aligarh, UP–202002, India.
Tel.: +91 9358255791
E–mail address: tsartaj62@yahoo.com (S. Tabassum)

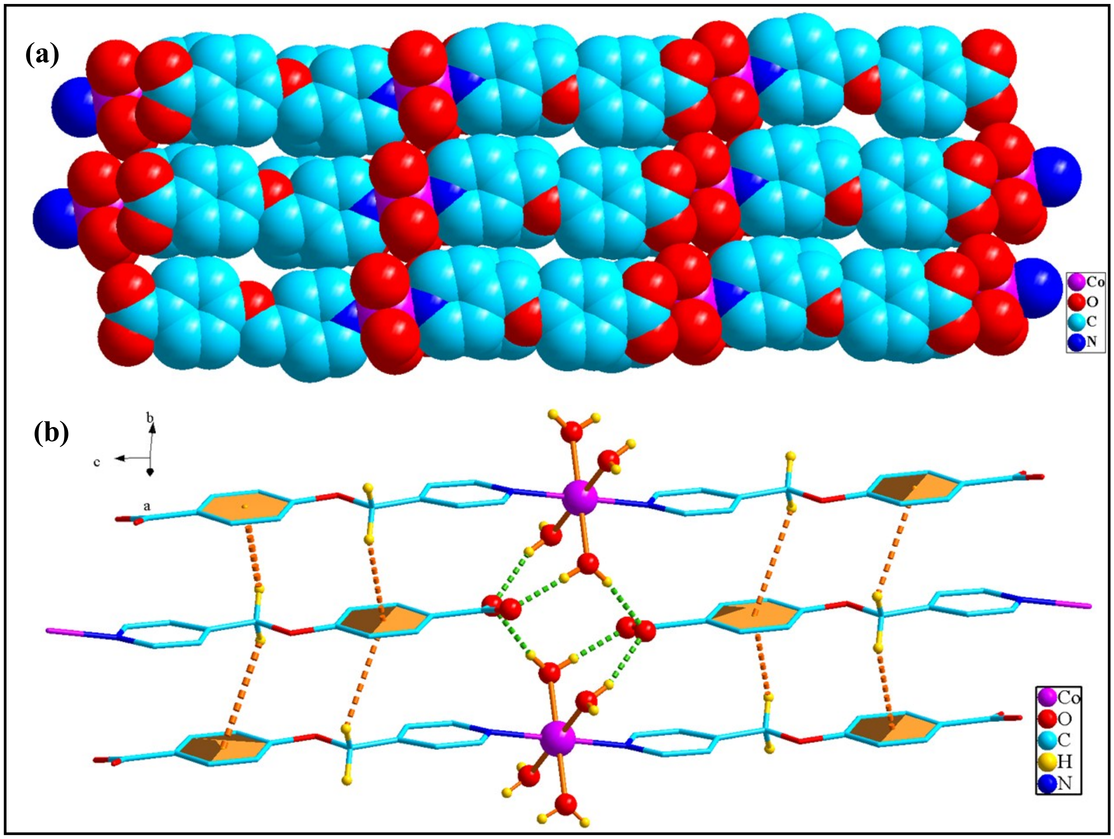

Fig. S1. Diagrammatic representation of (a) 3D packing (in space fill model) (b) H–bonding and $CH-\pi$ interactions in complex **1**.

TGA and PXRD Studies

In order to examine the thermal stabilities of the complex, thermal analysis was carried out in a N_2 atmosphere at the rate of 5 °C per minute. It shows a weight loss of ~12.48% (expected = 12.27%) within the temperature range 160–200 °C that corresponds to the release of four coordinated water molecules. The complex is found to be stable up to 300 °C, where after the framework starts to decompose (Fig. S2).

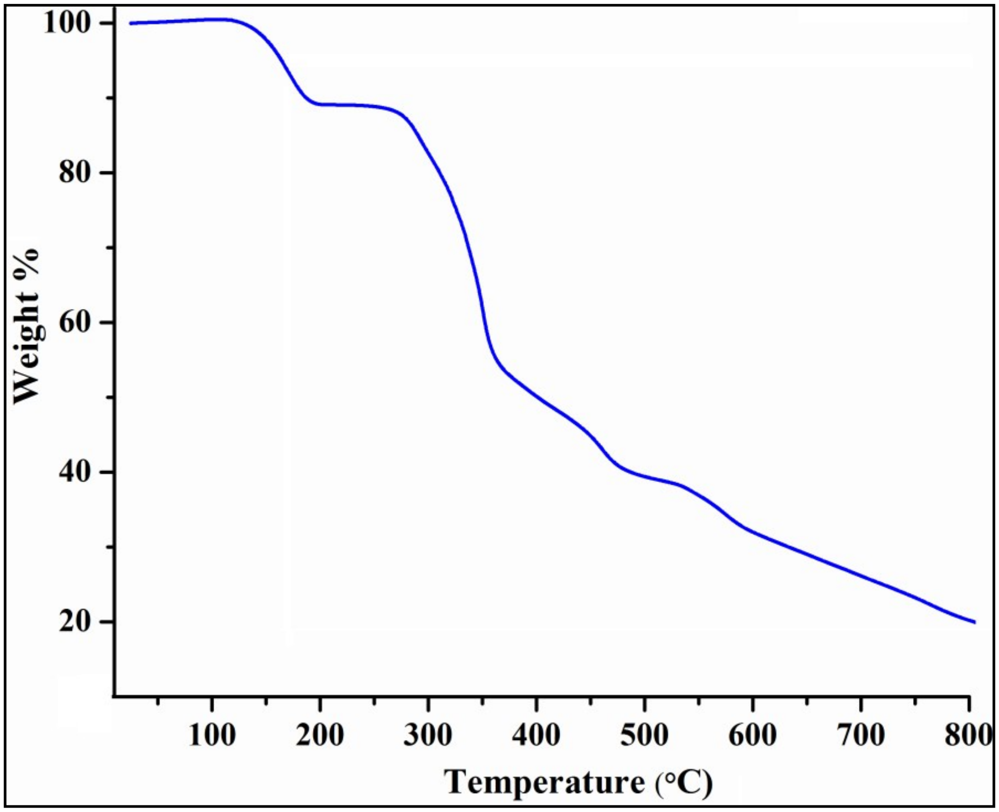

Fig S2. Thermogravimetric analysis of Complex **1**

A powder X–ray diffraction (PXRD) pattern of the complex matches well with the simulated patterns obtained from the single crystal X–ray data (Fig. S3). This confirms that the crystals are truly representative of the bulk phase. The differences in intensity could be due to the different orientation of the powder samples.

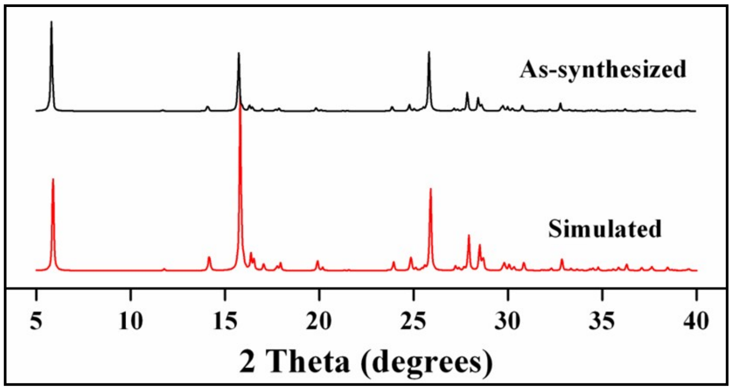

Fig S3. PXRD plot of Complex **1**

Theoretical Investigations

The optimized structure shows a significantly large resemblance with the X–ray crystal structure. The Mulliken spin density on the metal centre was found to be zero. This is consistent with the 2+ oxidation state of cobalt (d^7). The electrons in HOMO are stabilized relative to LUMO by an energy of 0.238 eV. Based on the distribution of electron density in HOMO and LUMO (Figs S4–S6), it is clearly evident that during an absorption process, the charge is shifted from HOMO predominantly on pyridyl moiety to LUMO which predominantly located on the carboxylate.

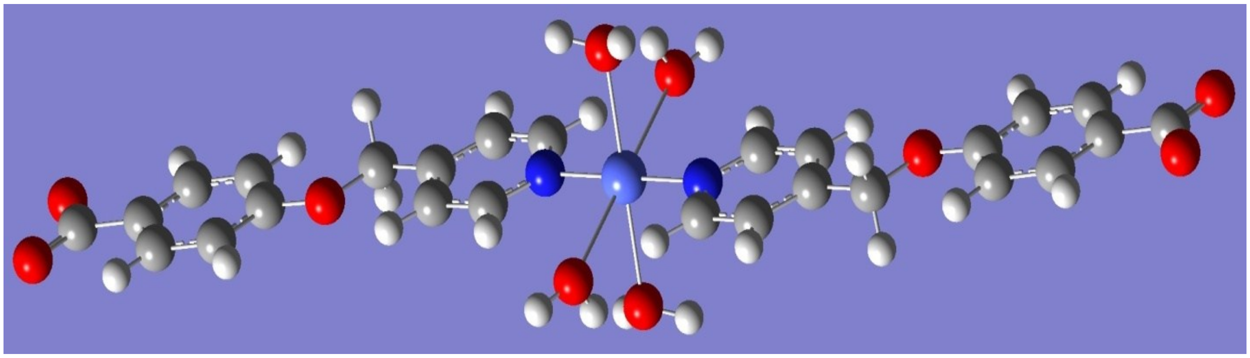

Fig. S4. The optimized geometrical structure of complex **1**.

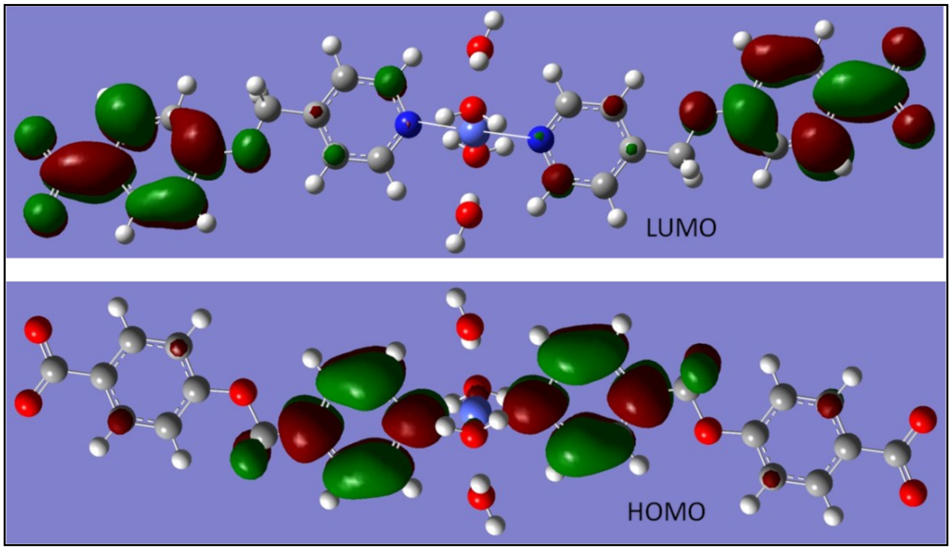

Fig. S5. The atomic orbital HOMO and LUMO compositions of the frontier molecular orbital for complex **1**.

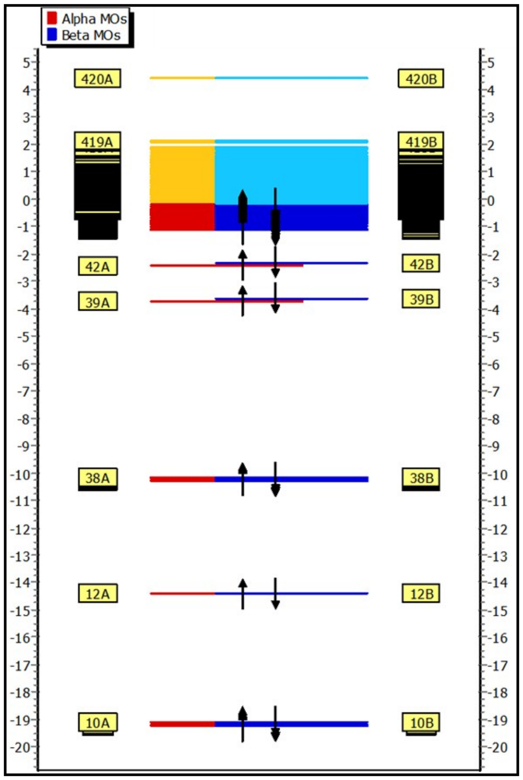

Fig. S6. Schematic representation of MOs energy levels for complex **1**.

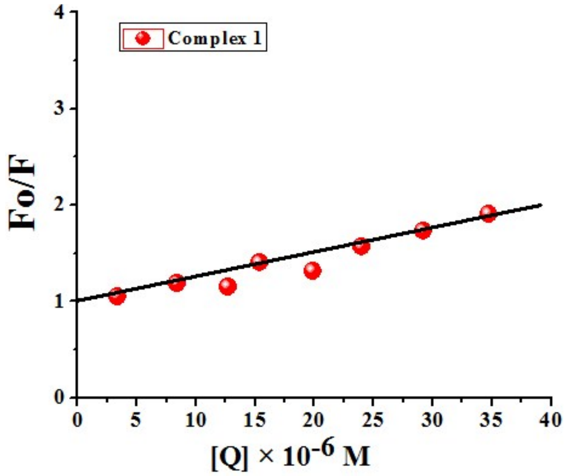

Fig. S7. Stern–Volmer plots showing HSA tryptophan quenching caused by complex **1** at room temperature (pH 7.40, λ_{ex} = 295 nm, λ_{em} = 332 nm).

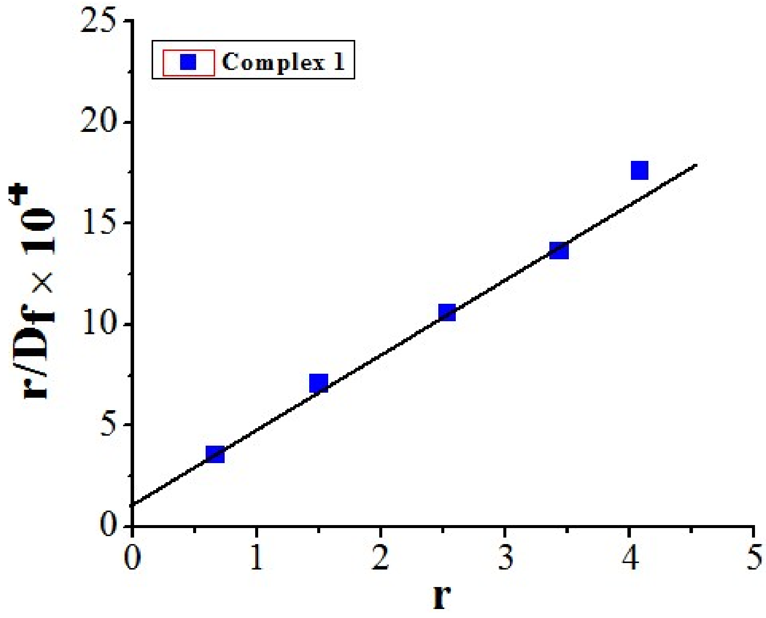

Fig. S8. Logarithmic plot of the fluorescence quenching of HSA for the calculation of binding constant (K) and number of binding sites (n) for complex **1** HSA at room temperature.

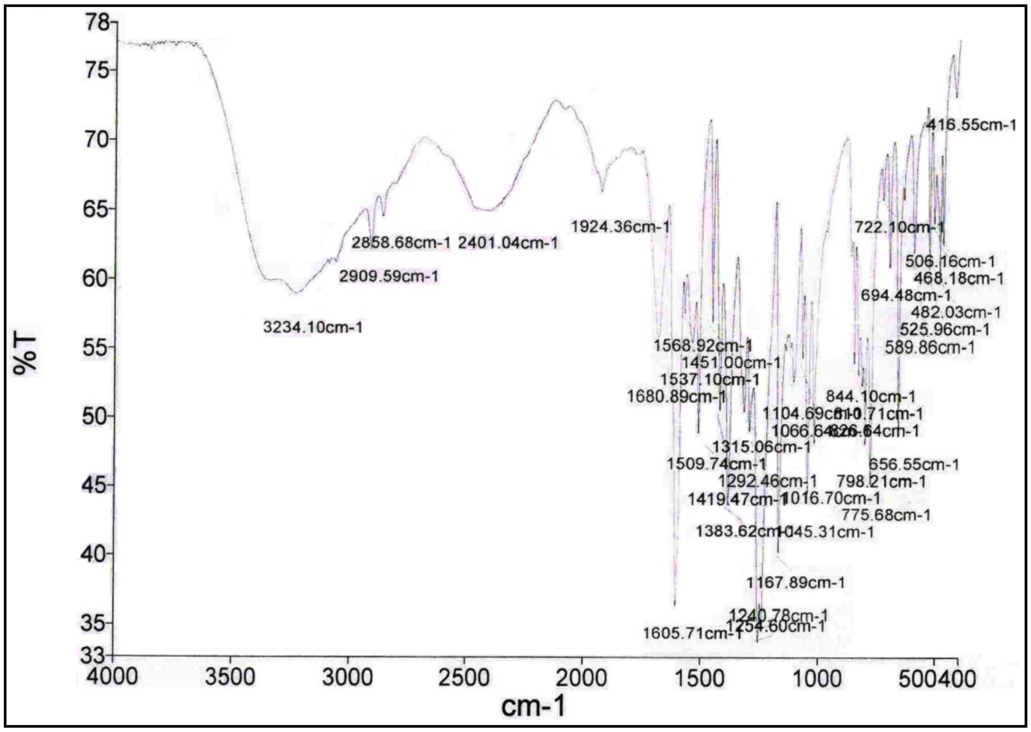

Fig S9. IR spectrum of Complex **1.**

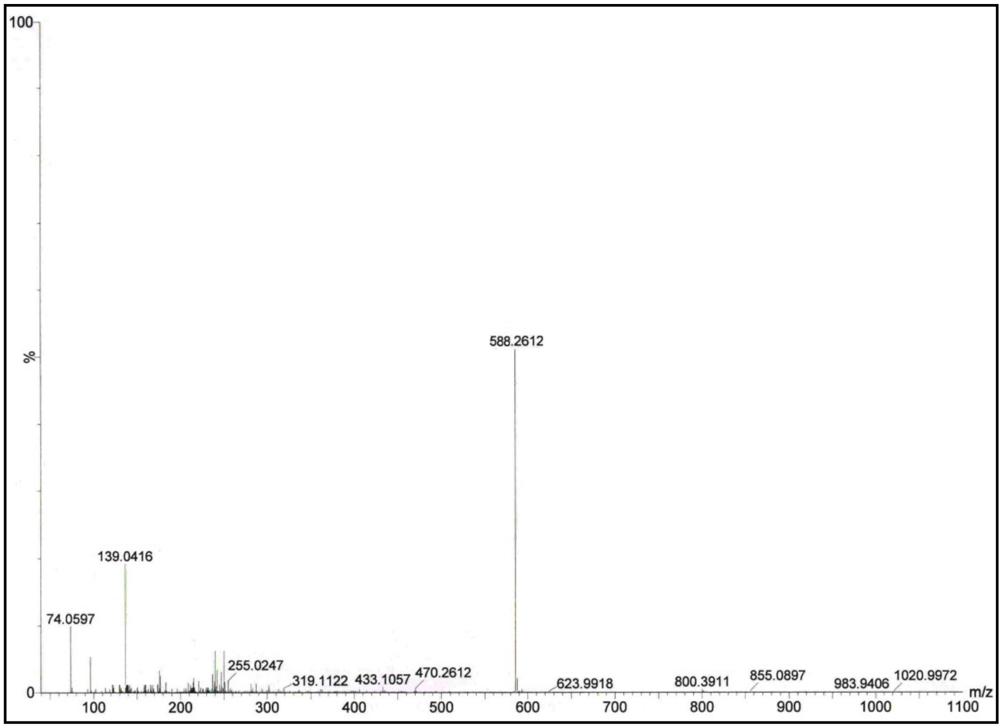

Fig S10. ESI-MS spectrum of Complex **1**.

Table S1. Selected bond distances(Å) and bond angles(°) in complex **1**

Co1 O1 2.098(2)	Co1 O2 2.123(3)	Co1 N1 2.129(3)
O1 Co1 O1 180.00(2)	O1 Co1 O2 94.63(11)	O1 Co1 O2 85.37(11)
O2 Co1 O2 180.00(11)	O1 Co1 N1 88.46(10)	O1 Co1 N1 91.54(10)
O2 Co1 N1 88.88(10)	O2 Co1 N1 91.12(10)	N1 Co1 N1 180.00(1)

Theoretical Calculations

Quantum chemical calculations were pursued at the level of density functional theory (DFT) to calculate the optimized geometry. Gaussian 09 software package was used to find the optimized energies, energy of frontier molecular orbitals (HOMO and LUMO) with B3LYP/6–31+g(d,p) basis function.[1] Optimizations were carried out employing X–ray coordinates using Becke's three parameter hybrid exchange functional with the Lee–Yang–Parr correlation function (B3LYP).[2–4] Hay and wadt basis set LANL2DZ was used for zinc metal centre while for rest of the atoms 6–31G basis set was employed. Tight convergence criteria were used with the self–consistent field "tight" option in all calculations, in order to ensure sufficiently well convergence. The authenticity of the final optimized geometry was confirmed by the absence of any imaginary frequency values, and also the convergence in force and maximum displacement further established the occurrence of ground state minima.

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