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STRUCTURE AND THERMAL REACTIVITY OF A NEW SEVEN COORDINATED HYDRAZINIUM (ETHYLENEDIAMINETETRAACETATO)AQUO COBALTATE(II) DEHYDRATE; HIRSHFELD SURFACE ANALYSIS AND DNA BINDING STUDIES

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Abstract

A novel 7-coordinated hydrated cobalt(II) ethylenediaminetetraacetate complex with hydrazinium cation, has been synthesized in aqueous medium and its composition has been assigned as $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$ on the basis of hydrazine, CHN and metal analyses and characterized by conductivity and magnetic measurement, UV-visible and infrared spectral and crystal studies. The thermal degradation studies reveal the presence of two types of water molecules viz., coordinated and lattice water molecules. Hydrazinium cation is present outside the coordination sphere as charge neutralizing species. X-ray single crystal structure reveals that the cobalt(II) ion is seven coordinated and $edta^{4-}$ act as a hexadentate chelating ligand. One water molecule occupies the seventh site resulting in the pentagonal bipyrimidal geometry. Hirshfeld surface analysis and fingerprint plots revealed influence of weak or non bonding interactions in crystal packing of complex. The DNA binding property of the complex with calf-thymus DNA has been investigated using electronic absorption spectrophotometry and the binding constant K_b calculated is in favour of strong interaction between the complex and DNA.

Keywords: 7-coordination; cobalt(II); TG-DTA; single crystals; hirshfeld surface; DNA binding.

Introduction

Hydrazine based metal-edta complexes are of growing interest due to their structure, thermal reactivity and biological activity. Several monohydrazinium metal-edta complexes of transition metal ion such as Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}[1-4] and rare earth metal-edta complexes such as Ln^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+}, Tb^{3+} [5-8] have been investigated in detail and the structures of most of the complexes have been determined. However, dihydrazinium metal-edta complexes are score and only a few are available in the literature. The interest in these complexes are due to the presence of hydrazinium cation which can act as positively charged ligand or may present either as ion species or coordinated to central metal ion. Furthermore, the presence of endotherm N-N bond in $N_2H_5^+$ cation could be exploited during the thermal degradation of these complexes which are expected to yield pure metal oxide at lower temperatures. In all the above transition metal complexes, the metal ions form complexes with mono protonated pentadentate edta anion ($Hedta^{3-}$) while the lanthanide ions from complexes with hexadentate $edta^{4-}$ complexes. However, cobalt-edta complexes with hydrazine are rare due to the hygroscopic nature and highly water soluble nature which makes them difficult to isolate from aqueous solution in the solid state. During our present investigations, we were able to isolate new seven coordinated hydrazinium cobalt(II) ethylenediaminetetraacetate hydrate as a single crystal. And hence, we wish to report the synthesis, structure, spectral, thermal, hirshfeld surface analysis and DNA binding properties of complex.

Experimental section

Materials and methods

All the chemicals used for the synthesis and analyses were of analytical reagent grade. Double distilled water was used for the preparation and analysis of the complex. Calf thymus DNA (CT-DNA) was purchased from Merck and stored at 4 °C.

Physical measurement

The hydrazine content present in the complex was determined volumetrically using KIO_3 solution (0.025 M) under Andrews's condition. The metal content was determined by EDTA complexometric titration after decomposing a known amount of the complex with concentrated nitric acid for several times [9-10]. The C, H and N analysis was carried out using a Perkin-Elmer (model 1240) CHN analyzer. The molar conductivity at room temperature was determined in conductivity water using a century digital conductivity meter model CC 601 and a dip type cell with a smooth platinum electrode. The room temperature magnetic susceptibility measurements were carried out with Gouy balance using $Hg[Co(SCN)_4]$ as a calibrant. UV-visible absorbance spectrum was recorded in the range 800-200 nm using Systronics double beam 2200 spectrophotometer. IR spectrum was recorded in the range of 4000-400 cm^{-1} by using Perkin-Elmer 597 spectrophotometer as KBr pellets. The simultaneous TG-DTA of the complex was performed on a SWITG/DTA 6200 thermal analyzer using 5 mg of the sample. The heating rate employed was 10 °C min^{-1} and aluminium cup was used as sample holder.

X-ray crystallography data collection and processing:

X-ray single crystal data for the complex was collected using Enruf-Nonius CAD-4 diffractometer with graphite monochromater and Mo-K_α radiation (λ=0.71073 Å). The structure was solved by the Patterson method and refined by applying full matrix least square techniques. Refinements were carried out using SHELXL-97 program [11-12]. Atomic scattering factors and anomalous dispersion collections were obtained from international tables for X-ray crystallography [13]. The structure model was drawn using ORTEP diagram.

Hirshfeld Surface Analysis

Hirshfeld surfaces [14-16] and the associated two-dimensional (2D) fingerprint plots were calculated using crystal explorer [17-20], with bond lengths to hydrogen atoms set to standard values [21]. For each point on the Hirshfeld isosurface, two distances, d_e (the distance from the point to the nearest nucleus external to the surface) and d_i (the distance to the nearest eight nucleus internal to the surface), are defined. The normalized contact distance d_{norm} based on d_e and d_i is given by,

$$d_{norm} = (d_i - r_i^{vdW}) / r_i^{vdW} + (d_e - r_e^{vdW}) / r_e^{vdW}$$

Where r_i^{vdW} and r_e^{vdW} are the Van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending on intermolecular contacts being shorter or longer than the Van der Waals separations. The parameter d_{norm} displays a surface with a red-white-blue color scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the Van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [22] and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

Fluorescence titration and three dimensional of cobalt(II) complex with CT-DNA

The fluorescence titration was conducted on spectrofluorometer JASCO – FP8200 instrument, with excitation at 236 nm. The concentration of cobalt(II) complex (10 µM) is kept constant (1 equiv.) and the solution was titrated with incremental addition of CT-DNA (10 µM) and emission was recorded from 246 nm to 750 nm.

All the 3D spectra were performed in the same fluorometer instrument with subjection of CT-DNA in presence and absence of cobalt(II) complex to simultaneous excitation and emission wavelength in three dimensional mode. Excitation range from 236 nm to 746 nm with regular interval of 5 nm and emission range from 200 nm to 750 nm wavelength with 2 nm regular interval.

DNA binding studies

Electronic absorption titration

All the experiments involving interaction of complex with CT-DNA was carried out in a buffer containing 5 mM of Tris(hydroxy-methyl)aminomethane and 50 mM of NaCl adjusted to pH 7.2 with hydrochloric acid. A solution of CT-DNA gave a ratio of UV absorbance of about 1.8–1.9 at 260 and 280 nm, indicating that the CT-DNA was sufficiently free of protein [23]. The CT-DNA concentration per nucleotide was determined by UV-spectrophotometer employing molar absorption coefficient 6600 M^{-1} cm^{-1} at 260 nm [24].

Absorption titrations were carried out at room temperature for determining the binding affinity between DNA and complexes. An appropriate amount of metal complex was dissolved in a solvent mixture of 1% H_2O and 99% Tris-HCl buffer. Absorption titration experiments were performed with the fixed concentration of the metal complex by gradually increasing the concentration of CT-DNA. From the absorption titration data, the binding constant (K_b) of the complex was determined from equation (1), through a plot of $[DNA]/(\varepsilon_a – \varepsilon_f)$ vs. [DNA].

$$[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f) \quad (1)$$

Where, [DNA] is the concentration of DNA, ε_a, ε_f and ε_b the apparent extinction coefficient (A_{obs}/[M]), the extinction coefficient for free metal complex (M), and the extinction coefficient for the free metal complex (M) in the fully bound form, respectively. In plots of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs. [DNA], K_b is given by the ratio of slope to intercept [25].

Preparation of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

The ligand dihydrazinium dihydrogenethylenediaminetetraacetate is prepared by the aqueous neutralization reaction between ethylenediaminetetraacetic acid and hydrazine hydrate in 1:2 molar ratios as reported earlier [26].

To an aqueous solution (50 mL) of cobalt(II) nitrate hexahydrate (2.91 g, 0.01 mol), an aqueous solution (50 mL) of dihydrazinium dihydrogenethylenediaminetetraacetate $(N_2H_5)_2[H_2edta]$, (7.04 g, 0.02 mol) was added at room temperature with constant stirring. The resulting clear solution was allowed to stand at room temperature for about 4 hrs. The colourless powder precipitated was removed and identified as ethylenediaminetetraaetatic acid. The resulting pink solution on slow evaporation at room temperature yielded pink crystals of the complex in a month time. Yield: 62%. Anal. Calc.: C, 25.70; H, 6.04; N, 17.98%. Found: C, 25.45; H, 5.95; N, 17.52%. N_2H_4 Found (Calc.): 12.48 (13.69) %. Co Found (Calc.): 1261 (12.10) %. IR (KBr): ν = 3450 (O–H), 1000 (N–N), 1600 $(COO^-)_{asym}$, 1380 $(COO^-)_{sym}$, 506 (M–O), 442 (M–N) cm^{-1}.

Results and discussion

Dihydrazinium ethylenediaminetetraacetatoaquocobaltate(II) dihydrate has been synthesized by the reaction between the ligand and cobalt(II) nitrate hexahydrate. The pink crystals obtained were collected and carefully stored in a vacuum desiccator. The complex is stable, slightly hygroscopic when exposed to air, soluble in water and insoluble in ethanol, ether and other organic solvent.

Though two hydrazinium cation and only one ethylenediaminetetraacetate ions are found in the complex, our attempt prepare hydrazine complex by using 1:1 ligand to metal(II) ratio always resulted in the formation of simple cobalt(II) dihydrogenethylenediaminetetatraacetate hydrate. Hence, excess of hydrazine is required for the preparation of hydrazine complex, the ligand is added in excess and the excess of H_4edta precipitated was removed prior to the crystallization of the hydrazine complex.

Furthermore, the same ratio with Ni(II), Cu(II), Zn(II) and Cd(II) has always resulted in the formation of mono hydrazinium complexes. In the present case only with Co(II) we were able to isolate a dihydrazinium complex. Such dihydrazinium complex with edta is new to the literature and the only complex isolated with $edta^{4-}$.

Characterization of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

The composition of the complex was assigned on the basis of hydrazine, metal and elemental analyses [27]. The observed values are in very good agreement with the theoretical values for the assigned composition.

Conductivity measurement

The conductivity of 0.001 mol of the complex in aqueous solution is found to be 220 mho cm^2 mol^{-1}. This value corresponds to the 1:2 type electrolytes. Hence, it is assumed that two hydrazinium cations could be outside the coordination sphere and the ionization takes place as follows,

$$(N_2H_5)_2[Co(edta)^{4-}(H_2O)]\ (H_2O)_2 \xrightarrow{H_2O} 2N_2H_5^+ + [Co(edta)(H_2O)]^{2-}$$

Comparatively low conductivity value observed than expected for three ions in aqueous solution may be due to the slower moment of the larger complex ion.

Magnetic moment and Electronic spectra

The observed magnetic moment of the cobalt complex is 4.9 B.M. For the Co^{2+} ion with three unpaired electron, the expected magnetic moment is around 3.87 B.M. The higher value is attributed to the spin-orbit coupling. Since the carboxylate ions are weaker ligands and hence high-spin complexes are always expected.

In the electronic spectrum, a broad band centered at 20,000 cm^{-1} was observed. This is usually expected for the octahedral Co(II) ion. However, the electronic spectrum does not provide conclusive evidence about the geometry of the complex [28]. The electronic spectrum of the complex is shown in Fig. 1.

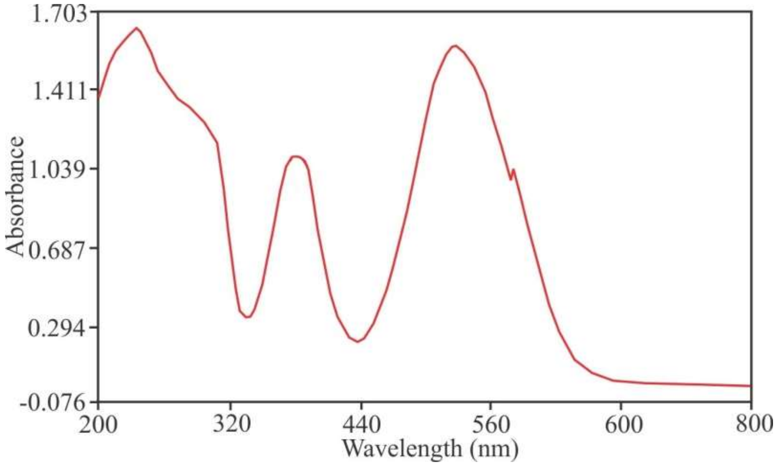

Fig. 1 Electronic spectra of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

Infrared spectrum

In the infrared spectrum of the complex, a broad band with splitting along with a sharp band is observed in the region 3200-3500 cm^{-1}. A sharp band at 3350 cm^{-1} is attributed to the presence of a coordinated water molecule. Other bands are due to the N-H and O-H stretchings of hydrazinium cation and lattice water molecules respectively.

Presence of hydrazinium cation in the complex was ascertained by the band in the region 960-1000 cm^{-1}. N-N stretching of the coordinated neutral hydrazine and non-coordinated hydrazinium cation shows a band between 960-970 cm^{-1} and for coordinated $N_2H_5^+$ ion is expected around 1000 cm^{-1} [29].

In the present case, a weak and sharp band is observed at 970 cm^{-1} which is assigned to the presence of non coordinated $N_2H_5^+$ cation. Presence of neutral hydrazinium molecules is rules out on the basis of analytical and conductivity studies. In the fingerprint region, several strong and sharp band are observed for the edta^{4-} ion. Hence, it is very difficult to assign these bands for the individual stretching and bending modes. However, two very strong and sharp bands at 1600 and 1380 cm^{-1} observed are assigned to $\square_{asym}$ and $\square_{sym}$ stretchings of monodentate carboxylate ions [30]. The IR spectrum of the complex is shown in Fig. 2.

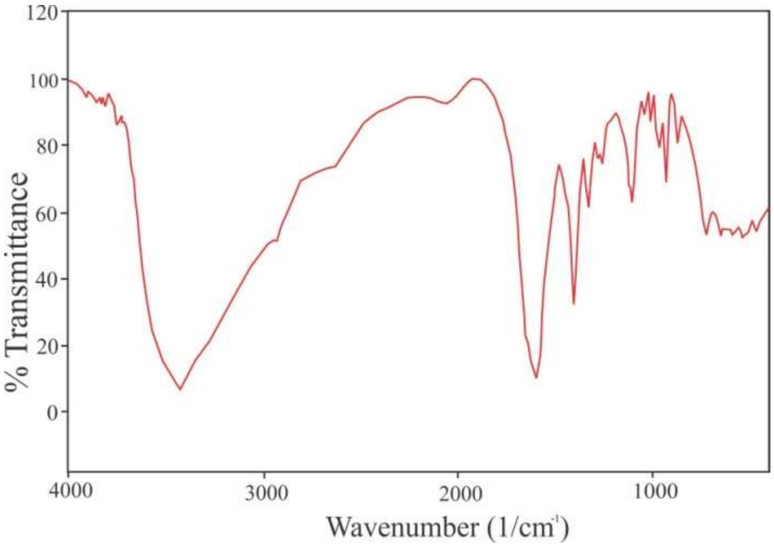

Fig. 2 IR Spectra of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

Thermal degradation studies

Thermal techniques such as TG and DTA are very important techniques which give several information about the coordination compounds especially with hydrazinium metal carboxylates. The presence of different types of water molecules (coordinated or lattice water molecules or both) can be easily determined by TG-DTA analysis. Beside these, the degradation pattern and final product formed can also be assigned from the thermal traces.

Simultaneous TG-DTA of the cobalt complex shows four stages of degradation. In the first stage below 90 °C with about 7.5 % weight loss is observed, which is attributed to the loss of two lattice water molecules. (Theoretical value: 7.70 %). A week and broad exotherm centered at 110 °C was observed in the DTA for this stage.

Another weak endotherm is observed at 262 °C for which TG shows 24.30 % weight loss. This corresponds to the dehydration of coordinated water molecule (Calc. 25.26 %). After dehydration two hydrazinium molecules are eliminated exothermally resulting in the formation of $[CoH_2edta]$ as an intermediate. This exothermic degradation is quite expected due to the presence of N-N bonds in hydrazinium cations which is endothermic in nature. Finally from 240-400°C the intermediate undergoes exothermic decomposition to yield Co_2O_3 as the final product. The formation of this oxide has been confirmed by the TG weight loss (Obs.: 84.10 %; Calc.: 83.46 %) and X-ray powder diffraction pattern. DTA show a weak and broad exotherm for the last stage. The simultaneous TG-DTA trace of the complex is shown in Fig 3.

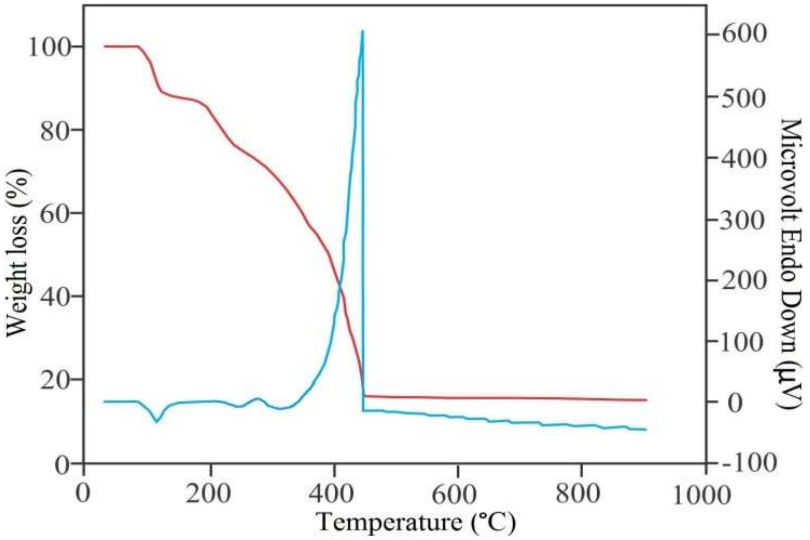

Fig. 3 TG-DTA of the complex $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

Crystal structure of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

In the present case Co(II) ion shows interesting coordination behavior. Co(II) ion is seven coordinated, and it is worth to mention here that this is the first report in hydrazinium chemistry with seven coordinated transition metal ion with +2 oxidation state. Despite the presence of two hydrazinium cations which are capable of coordination in the present case cobalt(II) ion prefers water molecule rather than $N_2H_5^+$ ion. This behavior is attributed to the fact that it is not the cobalt ion which seeks water, then hydrazinium cation, but the large number of water molecules in aqueous solution, compete and succeeds to coordinate with Co(II) ion when compared to fewer number of hydrazinium cations present in the reaction mixture.

The ORTEP and packing diagram of the complex are given in Fig. 4 and 5 respectively. The crystal data and bond distances and bond angles are given in Table 1 and 2 respectively. The hydrogen bond interactions are given Table 3.

The ORTEP diagram clearly reveals that the complex is made up of three discrete ions such as two hydrazinium cation and one complex anion. Among the three water molecules one is present in the primary coordination sphere and two other present in the secondary spheres which are involved in the hydrogen bonding interaction. Thermal data also support the presence of two types of water molecules.

The complex crystallized as in with C2/c space group. The observed density (1.691 mg/m^3) is comparable with the experimental value (1.72 mg/m^3). There are four molecules per unit cell (z=4). Four carboxylate oxygen atoms and two nitrogen atoms are coordinated to the Co(II) ion and hence unlike previously reported nickel, copper, zinc and cadmium complexes in the present case the edta^{4-} acts as a hexadentate ligand and the carboxylate ions show monodentate coordination behavior. One water molecule is coordinated and differs from two other as observed from their O-H bond distances. The complex is expected to be pentagonal bipyramidal with two nitrogen atom and three carboxylate oxygen atoms in the plane. The forth carboxylate oxygen atom and the oxygen atom of the water molecule are perpendicular to the plane, which is further confirmed by their longer and weaker bonds. Both hydrazinium cations and non-coordinated water molecules are involved in hydrogen bonding which stabilizes the structure of the complex. Our literature survey reveals that the cobalt complex isolated with aqueous medium is strongly hygroscopic in nature and very difficult to store and solve the structure. Only a few cobalt complexes with hydrazinium cation were isolated and their structures were solved so far [31].

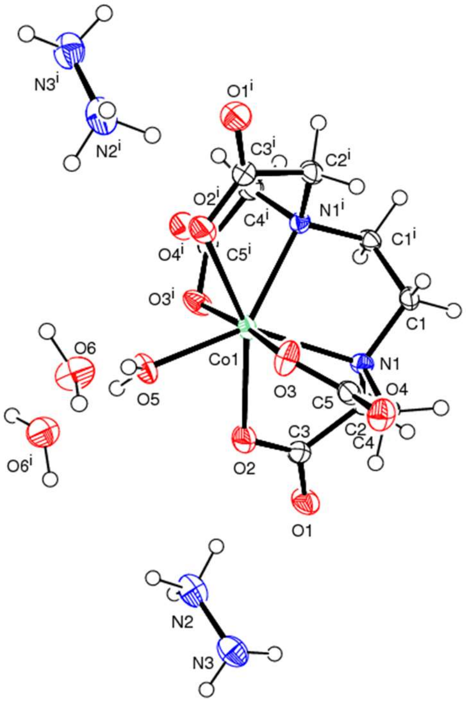

Fig. 4 ORTEP diagram of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

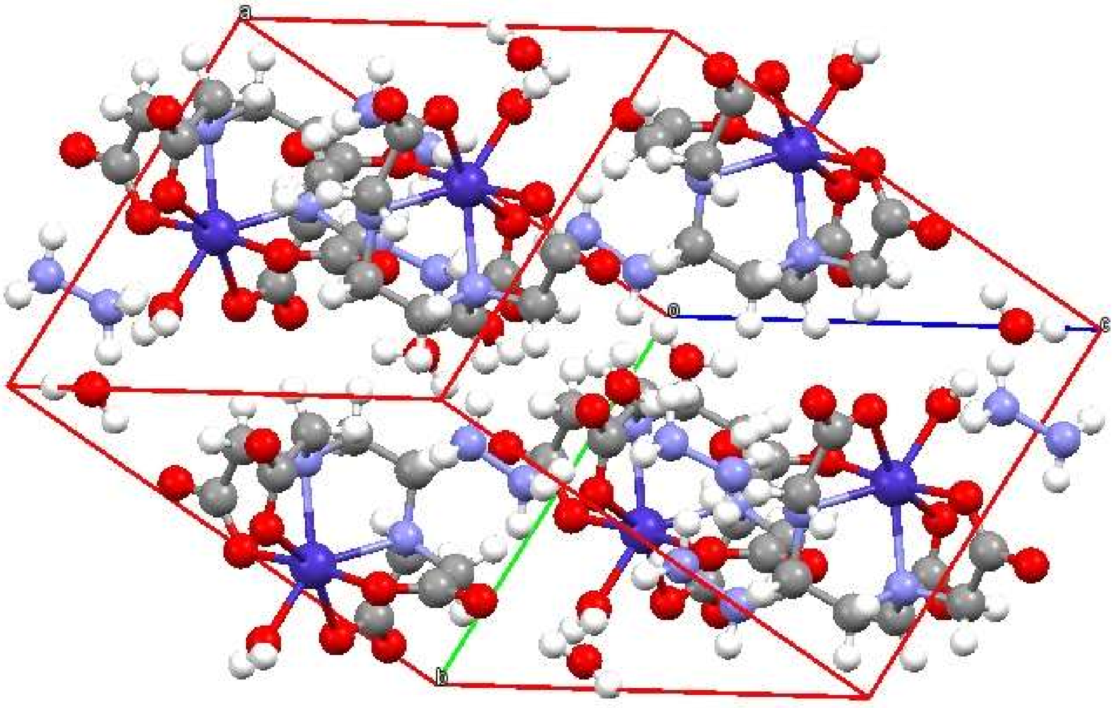

Fig. 5 Packing diagram of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

Table 1 Crystal data and structure refinement for $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

CCDC No		
Empirical formula	C_{10} H_{28} Co N_6 O_{11}	
Formula weight	467.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 11.1914(8) Å	□ = 90°.
	b = 9.6541(6) Å	□ = 107.569(2)°.
	c = 17.8173(12) Å	□ = 90°.
Volume	1835.2(2) $Å^3$	
Z	4	
Density (calculated)	1.691 Mg/m^3	
Absorption coefficient	1.006 mm^{-1}	
F(000)	980	
Crystal size	0.250 x 0.200 x 0.100 mm^3	
Theta range for data collection	2.398 to 24.997°.	
Index ranges	-13<=h<=13, -11<=k<=11, -21<=l<=21	
Reflections collected	11287	
Independent reflections	1624 [R(int) = 0.0235]	
Completeness to theta = 24.997°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7466 and 0.6337	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1624 / 13 / 157	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0711	
R indices (all data)	R1 = 0.0295, wR2 = 0.0731	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.760 and -0.266 e.$Å^{-3}$	

Table 2 Bond length and bond angles for $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

Bond lengths[Å]		angles [°]	
N(1)-Co(1)	2.2425(16)	C(2)-N(1)-Co(1)	110.72(12)
O(2)-Co(1)	2.3835(15)	C(4)-N(1)-Co(1)	107.15(11)
O(3)-Co(1)	2.1055(14)	C(1)-N(1)-Co(1)	108.30(11)
O(5)-Co(1)	2.047(2)	C(3)-O(2)-Co(1)	115.52(13)
Co(1)-O(3)#1	2.1055(14)	C(5)-O(3)-Co(1)	119.21(12)

Co(1)-N(1)#1	2.2424(16)	Co(1)-O(5)-H(5A)	122.6(19)
Co(1)-O(2)#1	2.3835(15)	O(5)-Co(1)-O(3)#1	86.83(4)
		O(5)-Co(1)-O(3)	86.83(4)
		O(3)#1-Co(1)-O(3)	173.66(8)
		O(5)-Co(1)-N(1)#1	140.71(4)
		O(3)#1-Co(1)-N(1)#1	76.72(5)
		O(3)-Co(1)-N(1)#1	108.38(6)
		O(5)-Co(1)-N(1)	140.71(4)
		O(3)#1-Co(1)-N(1)	108.38(6)
		O(3)-Co(1)-N(1)	76.72(5)
		N(1)#1-Co(1)-N(1)	78.59(8)
		O(5)-Co(1)-O(2)	78.71(4)
		O(3)#1-Co(1)-O(2)	75.83(6)
		O(3)-Co(1)-O(2)	102.89(6)
		N(1)#1-Co(1)-O(2)	129.18(5)
		N(1)-Co(1)-O(2)	70.81(5)
		O(5)-Co(1)-O(2)#1	78.71(4)
		O(3)#1-Co(1)-O(2)#1	102.89(6)
		O(3)-Co(1)-O(2)#1	75.83(6)
		N(1)#1-Co(1)-O(2)#1	70.81(5)
		N(1)-Co(1)-O(2)#1	129.18(5)
		O(2)-Co(1)-O(2)#1	157.41(7)

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

Table 3 Hydrogen bonds for $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4A)...O(2)#2	0.97	2.48	3.452(3)	175.9
N(2)-H(2C)...O(4)#3	0.957(16)	1.910(16)	2.834(3)	161(2)
N(2)-H(2D)...O(2)#4	0.939(16)	2.46(2)	3.269(3)	144(2)
N(2)-H(2D)...O(3)#5	0.939(16)	2.19(2)	2.885(2)	130(2)
N(2)-H(2E)...O(1)	0.957(16)	1.912(19)	2.738(2)	143(2)
N(3)-H(3A)...O(1)#6	0.888(16)	2.272(17)	3.153(3)	171(2)
N(3)-H(3B)...O(4)#5	0.896(17)	2.105(18)	2.991(2)	170(3)
O(5)-H(5A)...O(6)	0.840(16)	1.879(17)	2.710(2)	170(3)
O(6)-H(6A)...O(1)#3	0.852(17)	2.191(18)	2.998(2)	158(3)
O(6)-H(6B)...O(4)#7	0.885(17)	1.949(17)	2.826(2)	171(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 -x+1/2,y-1/2,-z+1/2 #3 -x+1/2,y+1/2,-z+1/2

#4 -x+1/2,-y+5/2,-z #5 x-1/2,-y+5/2,z-1/2 #6 -x,-y+2,-z
#7 x+1/2,y+1/2,z

Hirshfeld surface analysis

Hirshfeld surface analysis is powerful tool to investigate the intermolecular interaction. The $d_{(norm)}$, shape index and curvedness hirshfeld surfaces and fingerprint plots were generated for the present compound. The $d_{(norm)}$ maped on hirshfeld surface and the 2D fingerprint plots of the intermolecular interactions are shown in Fig. 6. O ··· H-O intermolecular interactions are one of the strong contacts due to the presence of several n-H···O and O-H···O hydrogen bonds. The O-H···O hydrogen bonding is absorbed between lattice water, coordinated water and carboxylate oxygen and N-H···O hydrogen bonding is seen between outer sphere hydrazinium ion and water or carboxylates oxygen. This analysis shows that O···H intermolecular links contribute 43.2 % to the overall crystal packing. The next most important interaction is H···H link contributing 37.2 % O···O, C···O, C···H and C···C interaction shows very weak intermolecular contacts. Fig. 7.

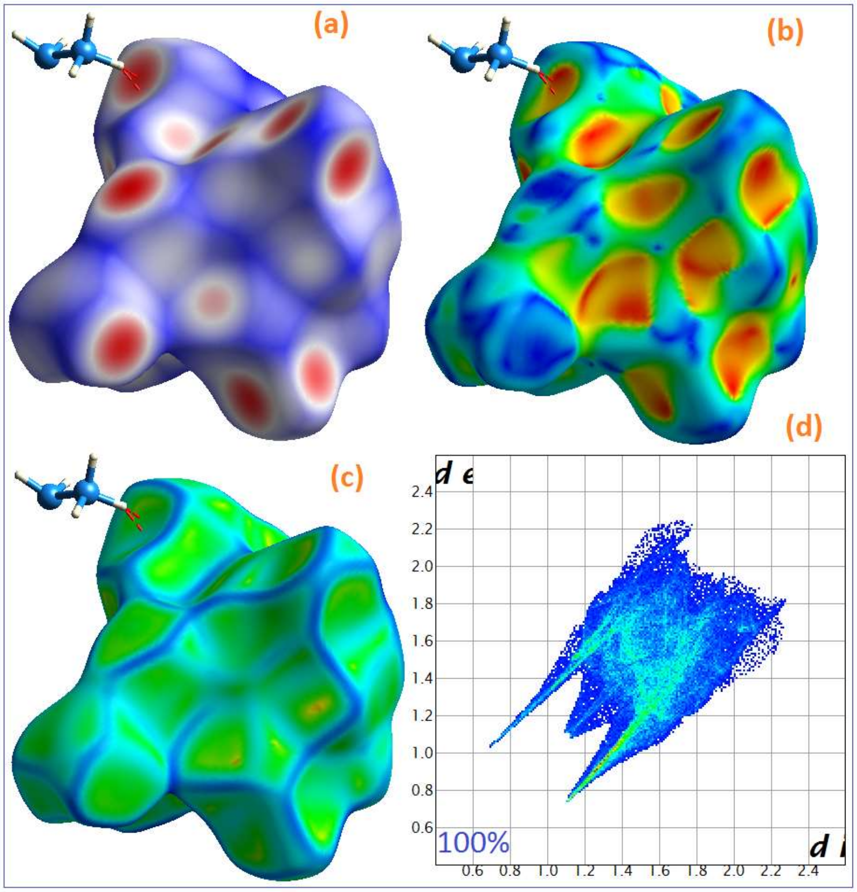

Fig. 6. (a) $d_{(norm)}$, (b) shape index, (c) Curvedness on the hirshfeld surface intermolecular forces belong the title compound, (d) 2D fingerprint (100 %)

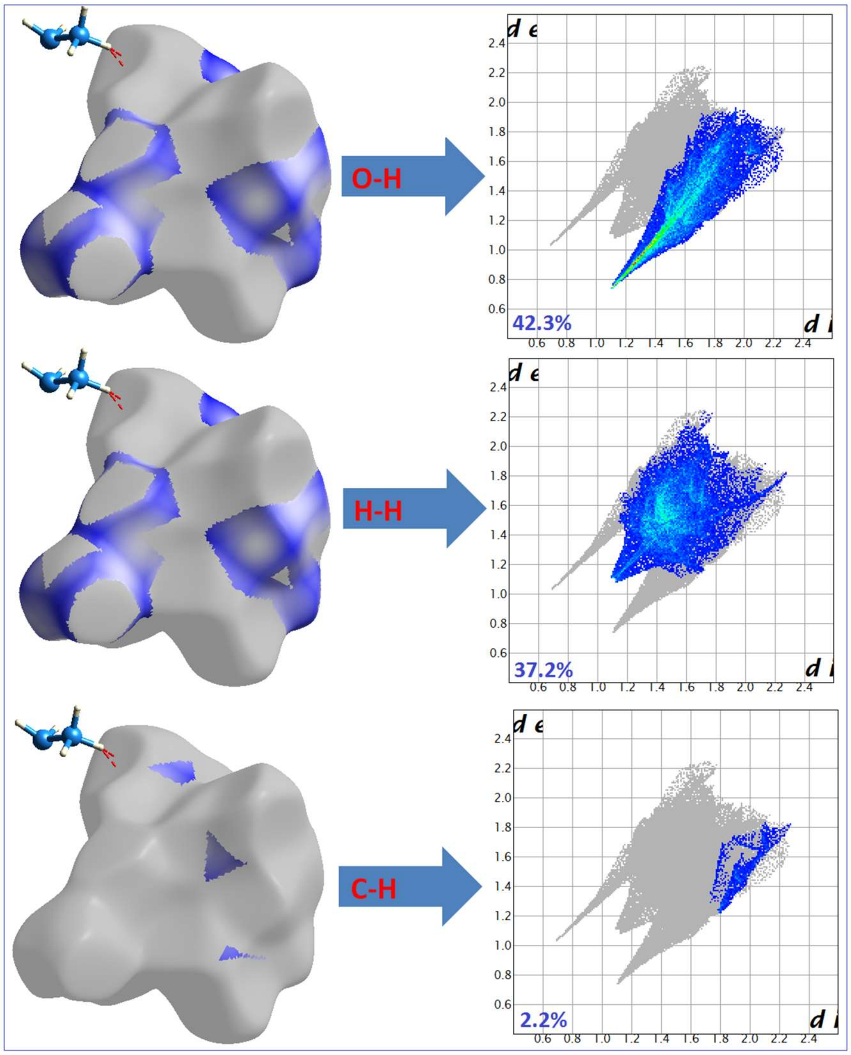

Fig. 7. Two dimentional fingerprint plot with a d(norm) view.

Three Dimensional Fluorescence Spectral studies

Three dimensional fluorescence spectra was performed for understanding the micro environmental and conformational changes occurring in Calf Thymus DNA upon interaction with newly synthesized **$N_2H_5[Co(edta)].2.5H_2O$** complex. The CT-DNA was subjected to 3D fluorescence spectral analysis before and after the addition of our copper complex with excitation from 236 nm to 746 nm and monitoring at 200 nm to 750 nm emission range.

The free CT-DNA exhibits four characteristic peaks Peak A, Peak 1, Peak 2 and Peak B, where Peak A and Peak B represents the Rayleigh first and second order scattering peak and the Peak 1 and Peak 2 corresponds to the tryptophan and tyrosine residue of proteins. The 3D spectrum of CT-DNA on addition of cobalt(II) complex shows four characteristics peaks of CT-DNA accompanied with new 3D peak with low intensity.

The 3D fluorescence spectral plot and its colour and line contour plot are depicted in Fig. 14., the first and second order Rayleigh scattering peak of CT-DNA get slightly blue shift and decreased in fluorescence intensity, shows the interaction of complex with the DNA molecule through increase in molecular diameter of macromolecule which allows increasing scattering effect. Upon addition of the complex, Peak 1 of the CT-DNA characteristics band of tryptophan and tyrosine represents the n-π* transition peak and peak 2 corresponds to the polypeptide backbone π-π* transition band that extensively quenched in intensity with slight shift, and broadening of band due to perturbation upon interaction of CT-DNA with complex.

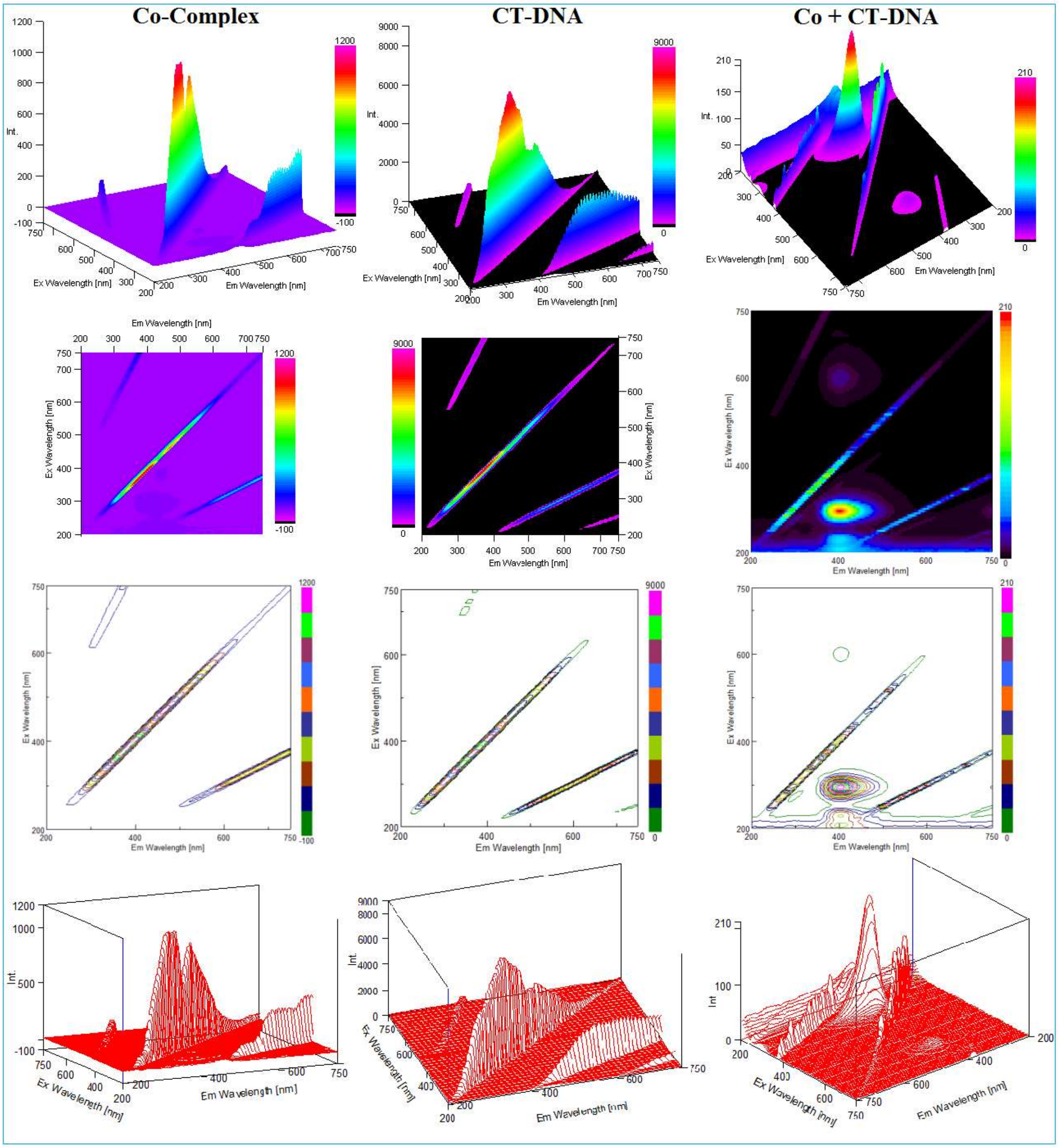

Fig. . Three-dimensional fluorescence spectra of DNA in the absence and the presence of cobalt complex (pH 7.4, 298 K, [DNA]=10 μM, [Complex]=10 μM).

DNA binding studies

Electronic absorption titration

The interaction of cobalt complex with CT-DNA was investigated using electronic absorption titration. The absorption spectra of the complex in the presence and absence of CT-DNA is shown in Fig. 8. The complex shows hyperchromic effect accompanied by a moderate blue shift of 1-2 nm which indicates the stabilization of the DNA helix [32, 33]. The hyperchromic effect is also due to the electrostatic interaction between positively charged cation and the negatively charged phosphate backbone at the periphery of the double helix-CT-DNA [34]. The binding constant K_b was calculated using Eq. 1 and found to be 4.58×10^4 M^{-1}. The K_b value shows that there is a strong interaction between the complex and DNA.

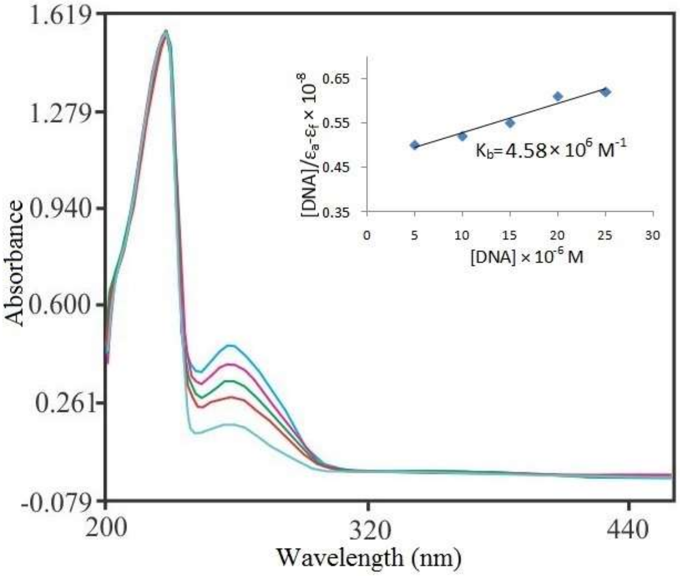

Fig. 8 DNA binding for $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$

Conclusion

Dihydrazinium ethylenediaminetetraacetatoaquocobaltate(II) dihydrate has been synthesized in aqueous medium and isolated as a single crystal.

Conductivity, spectral and thermal studies of the complex reveal that hydrazinium cations are ionic in nature and one water molecule is coordinated to Co(II) ion.

Thermal data is in accordance with the presence of two types of water molecules viz., coordinated and lattice water molecules. Simultaneous TG-DTA trace shows multiple step degradation and the final product is found to be Co_2O_3.

X-ray crystal data and ORTEP diagram show that Co(II) is seven coordinated with hexadentate $edta^{4-}$ ion and one coordinated water molecule. Two lattice water molecules and hydrazinium cation are in the secondary coordination sphere and involved in the hydrogen bonding interaction.

Hirshfeld surface theoretical analysis confirmed the formation of several polar and non-polar intermolecular short contacts in the crystal lattice of $(N_2H_5)_2[Co(edta)(H_2O)](H_2O)_2$.

DNA binding studies and binding constant, K_b are in accordance with the strong interaction between the complex and DNA.

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