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# Formation of H-bonding networks in the solid state structure of a trinuclear cobalt(III/II/III) complex with N<sub>2</sub>O<sub>2</sub> donor Schiff base ligand and glutaric acid as bridging co-ligand: synthesis, structure and DFT study†

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A trinuclear linear mixed-valence centrosymmetric cobalt(III)-cobalt(II)-cobalt(III) complex, [Co<sup>II</sup>{(μ-L)(μ-Hglu)Co<sup>III</sup>(OH<sub>2</sub>)<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O has been synthesized during tetradentate N<sub>2</sub>O<sub>2</sub> donor 'Schiff base' ligand, H<sub>2</sub>L {N,N'-bis(salicylidene)-1,3-diaminopropane} and glutaric acid (H<sub>2</sub>glu) as anionic co-ligand. The complex has been characterized by spectroscopic measurements and its solid state structure has been determined by single crystal X-ray diffraction analysis. The supra-molecular assembly formed by the hydrogen bonding interactions in the solid state of the complex has been analysed using DFT calculations.

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## Introduction

The use of cobalt complexes in several biomimetic catalysis is well known.<sup>1–21</sup> Cobalt complexes have also been used to fabricate different opto-electronic devices.<sup>22,23</sup> The magnetic properties of cobalt complexes are also interesting.<sup>24–27</sup> On the other hand, the attractive bridging capacity of the phenolate oxygen atoms of salen type ligands has led synthetic inorganic chemists and material scientist to synthesize and characterize high nuclearity cobalt complexes with these salen type ligands.<sup>28–30</sup> The complexes have been used as important magnetic materials.<sup>31,32</sup> Cobalt-salen related systems may catalyze the oxygenation of organic molecules and may be used as antiviral agents.<sup>1,33–45</sup> They have also been used to mimic several enzymes.<sup>38–45</sup> These types of promising applications of salen type complexes have attracted our attention for the synthesis of transition metal compounds of salen type N<sub>2</sub>O<sub>2</sub> donor Schiff base ligands.

Water is essential for many biological and chemical reactions in any living body.<sup>46–49</sup> Chemists, micro-biologists and theoretical chemists are trying to understand the behavior of

solid and liquid water at the molecular level since long.<sup>50</sup> To achieve a more precise narrative of the properties of bulk water at the molecular level, determination of the accurate structural data of various hydrogen-bonded water aggregations is necessary, where water clusters may assist the movement of protons along the H-bonded chain.<sup>51</sup> To investigate the stabilization of hydrogen-bonded water clusters or chains in the solid state structure of a transition metal complex is a very attracting area of research to the structural and theoretical chemists, as it may help to propose different models for the aggregations of water molecules in numerous *in vivo* pathways.<sup>52–56</sup> Different water clusters, *e.g.* tetramers, hexamers, octamers, decamers *etc.* found in a number of crystal hosts, have been extensively investigated.<sup>57–63</sup> A useful approach to the stabilization of water molecule aggregations is their capture within transition metal complex lattices formed by crystallization from aqueous solution.<sup>57,64–77</sup> To study the supramolecular architecture of transition metal complexes in its solid state structure is receiving immense attention now-a-days.<sup>78</sup> In the case of metal complexes the supramolecular components are most often held together by hydrogen bonding, π⋯π, C–H⋯π interactions, cation-π, anion-π *etc.*<sup>79–82</sup> Obviously, the most commonly used approach for engineering the supramolecular structure of these complexes is to employ hydrogen bonding.<sup>83–89</sup> Carboxylate bridged trinuclear mixed valence cobalt(III/II/III) complexes with salen type ligands constitute a special class for their interesting structures and each of synthesis.<sup>28,30,84,90</sup> The complexes could easily be prepared by adding cobalt(II) salt to a salen type ligand in presence of carboxylate co-ligands maintaining either 3 : 2 : 2 or 3 : 2 : 4 molar ratio. In the present work, we have isolated

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a linear, trinuclear, mixed valence cobalt(III/II/III) complex using a salen type quadridentate Schiff base ligand and di-carboxylic acid (glutaric acid) as the bridging co-ligand. Interestingly, the complex comes cationic in nature with counter perchlorate anions. Herein, we report the synthesis, characterization and supra-molecular assemblies of the cobalt(III/II/III) Schiff base complex,  $[\text{Co}^{\text{II}}\{(\mu\text{-L})(\mu\text{-Hglu})\text{Co}^{\text{III}}(\text{OH}_2)_2\}_2](\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  [ $\text{H}_2\text{L} = N,N'$ -bis(salicylidene)-1,3-diaminopropane,  $\text{H}_2\text{glu} = \text{glutaric acid}$ ]. We have performed the theoretical analysis of H-bonding networks involving the lattice water molecules, the perchlorate anions and the trinuclear cobalt(III/II/III) Schiff base complex and compared the strength of the H-bonds.

## Experimental section

### Materials

All chemicals were of reagent grade and used as purchased from Sigma-Aldrich without further purification.

### Synthesis of $[\text{Co}^{\text{II}}\{(\mu\text{-L})(\mu\text{-Hglu})\text{Co}^{\text{III}}(\text{OH}_2)_2\}_2](\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , $\{\text{H}_2\text{glu} = \text{glutaric acid}; \text{H}_2\text{L} = N,N'$ -bis(salicylidene)-1,3-diaminopropane}

$\text{H}_2\text{L}$  was synthesized as a yellow liquid by refluxing a methanol solution of 1,3-propanediamine (0.2 mL,  $\sim 2$  mmol) and salicylaldehyde (0.4 mL,  $\sim 4$  mmol) for *ca.* 1 h. It was not isolated and purified; but was used directly for the synthesis of the complex. A methanol (10 mL) solution of cobalt(II) perchlorate hexahydrate (1.10 g,  $\sim 3$  mmol) was added into the methanol solution of the Schiff base,  $\text{H}_2\text{L}$  and the mixture was stirred for 1 h. Then a methanol (5 mL) solution of glutaric acid ( $\text{C}_5\text{H}_8\text{O}_4$ ; 0.264 g,  $\sim 2$  mmol) was added to the reaction mixture with constant stirring. Few drops of  $\text{CH}_3\text{CN}$  have been added to the solution and the stirring was continued for about 2 h. Diffraction quality dark

brown single crystals were obtained after few days on slow evaporation of the solution in open atmosphere.

**Yield.** 0.80 g ( $\sim 60\%$ , based on cobalt), Anal. Calc. for  $\text{C}_{44}\text{H}_{60}\text{Co}_3\text{N}_4\text{Cl}_2\text{O}_{28}$  (FW = 1342.67): C, 39.36; H, 4.65; N, 4.17%; found: C, 39.39; H, 4.63; N, 4.18%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2960–2926 ( $\nu_{\text{C-H}}$ ); 1630–1552 ( $\nu_{\text{COO}^-}$ ); UV-Vis,  $\lambda_{\text{max}}$  590 nm [ $\epsilon_{\text{max}} = 5.0 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ ], 356 nm [ $\epsilon_{\text{max}} = 9.0 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ], 239 nm [ $\epsilon_{\text{max}} = 6.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ] ( $\text{CH}_3\text{CN}$ ). Magnetic moment,  $\mu = 5.1$  B. M.; crystal system: triclinic.

### Instrumentation

The details of different instruments are given in the ESI.† Crystallographic data and refinement details of the complex are given in Table 1. Important bond lengths and angles are listed in Tables 2 and 3, respectively.

### Computational details

The calculations reported herein were performed using the Turbomole 7.2 program.<sup>91</sup> The crystallographic coordinates were used for the calculations of the supramolecular assemblies. We used the crystallographic coordinates for the assemblies because we are interested in evaluating the interactions as they stand in the solid state. The level of theory used for the calculations was RI-BP86 (ref. 92 and 93)-D3 (ref. 94)/def2-TZVP.<sup>95,96</sup> The topological analysis of the electron density was carried out according to

Table 2 Selected bond lengths (Å) of the complex

|            |          |
|------------|----------|
| Co(1)–O(1) | 2.085(2) |
| Co(1)–O(2) | 2.103(2) |
| Co(1)–O(4) | 2.085(2) |
| Co(2)–O(1) | 1.924(2) |
| Co(2)–O(2) | 1.911(2) |
| Co(2)–O(3) | 1.889(2) |
| Co(2)–O(5) | 1.920(2) |
| Co(2)–N(1) | 1.928(2) |
| Co(2)–N(2) | 1.927(3) |

Table 3 Selected bond angles (°) of the complex<sup>a</sup>

|                 |            |
|-----------------|------------|
| O(1)–Co(1)–O(2) | 73.34(8)   |
| O(1)–Co(1)–O(4) | 85.69(8)   |
| O(2)–Co(1)–O(4) | 85.26(8)   |
| O(1)–Co(2)–O(2) | 81.43(9)   |
| O(1)–Co(2)–O(3) | 92.68(9)   |
| O(1)–Co(2)–O(5) | 92.14(11)  |
| O(1)–Co(2)–N(1) | 91.39(11)  |
| O(1)–Co(2)–N(2) | 172.89(10) |
| O(2)–Co(2)–O(3) | 92.94(9)   |
| O(2)–Co(2)–O(5) | 90.16(10)  |
| O(2)–Co(2)–N(1) | 172.82(11) |
| O(2)–Co(2)–N(2) | 91.53(11)  |
| O(3)–Co(2)–O(5) | 174.61(10) |
| O(3)–Co(2)–N(1) | 87.57(11)  |
| O(3)–Co(2)–N(2) | 86.68(11)  |
| O(5)–Co(2)–N(1) | 89.91(12)  |
| O(5)–Co(2)–N(2) | 88.83(12)  |
| N(1)–Co(2)–N(2) | 95.65(12)  |

<sup>a</sup> Symmetry transformation, \* =  $-x, 1 - y, -z$ .

Table 1 Crystal data and refinement details of the complex

|                                                                                               |                                                                           |
|-----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Formula                                                                                       | $\text{C}_{44}\text{H}_{60}\text{Co}_3\text{N}_4\text{Cl}_2\text{O}_{27}$ |
| Formula weight                                                                                | 1324.65                                                                   |
| Temperature (K)                                                                               | 293                                                                       |
| Crystal system                                                                                | Triclinic                                                                 |
| Space group                                                                                   | $P\bar{1}$                                                                |
| <i>a</i> (Å)                                                                                  | 10.4218(4)                                                                |
| <i>b</i> (Å)                                                                                  | 10.9812(4)                                                                |
| <i>c</i> (Å)                                                                                  | 12.6764(4)                                                                |
| $\alpha$ (°)                                                                                  | 104.684(1)                                                                |
| $\beta$ (°)                                                                                   | 97.921(1)                                                                 |
| $\gamma$ (°)                                                                                  | 100.105(1)                                                                |
| <i>Z</i>                                                                                      | 1                                                                         |
| <i>d</i> <sub>cal</sub> ( $\text{g cm}^{-3}$ )                                                | 1.62244                                                                   |
| $\mu$ ( $\text{mm}^{-1}$ )                                                                    | 1.098                                                                     |
| <i>F</i> (000)                                                                                | 683                                                                       |
| Total reflection                                                                              | 39 408                                                                    |
| Unique reflections                                                                            | 4814                                                                      |
| Observed data [ $I > 2\sigma(I)$ ]                                                            | 4359                                                                      |
| <i>R</i> (int)                                                                                | 0.036                                                                     |
| <sup>a</sup> <i>R</i> <sub>1</sub> , <sup>b</sup> <i>wR</i> <sub>2</sub> (all data)           | 0.0471, 0.1101                                                            |
| <sup>a</sup> <i>R</i> <sub>1</sub> , <sup>b</sup> <i>wR</i> <sub>2</sub> [ $I > 2\sigma(I)$ ] | 0.0424, 0.1071                                                            |

$$^a R_1 = \sum \|F_o\| / \sum \|F_c\|, ^b wR_2 = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2)^{1/2}.$$



the quantum theory of atoms in molecules (QTAIM) method proposed by Bader<sup>97</sup> and represented using the VMD program.<sup>98</sup> They were computed using the MultiWFN program<sup>99</sup> at the PB86-D3/def2-TZVP level of theory.

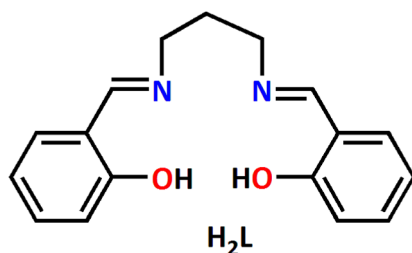
## Results and discussion

### Synthesis

Facile condensation of 1,3-propanediamine with salicylaldehyde in 1:2 molar ratio in methanol afforded a Schiff base ligand, H<sub>2</sub>L (where H indicates dissociable phenolic hydrogen atoms). The Schiff base was, however, not isolated and purified, but it was employed directly as a tetradentate chelating ligand in the present work for the synthesis of the complex. The structure of the ligand used is shown in Scheme 1.

The Schiff base, H<sub>2</sub>L, upon reaction with cobalt(II) perchlorate hexahydrate and glutaric acid in 2:3:2 ratio in methanol yielded the complex. Slow evaporation of mother liquor in open atmosphere gave brown crystals of the trinuclear mixed-valence cobalt(III/II/III) complex, as authenticated by X-ray structure determinations (*vide infra*). The synthetic procedure of the complex is shown in Scheme 2.

The precursor cobalt(II) perchlorate is partially oxidized by atmospheric oxygen during the course of the reaction. In order



Scheme 1 Schematic representation of the ligand used in the work.

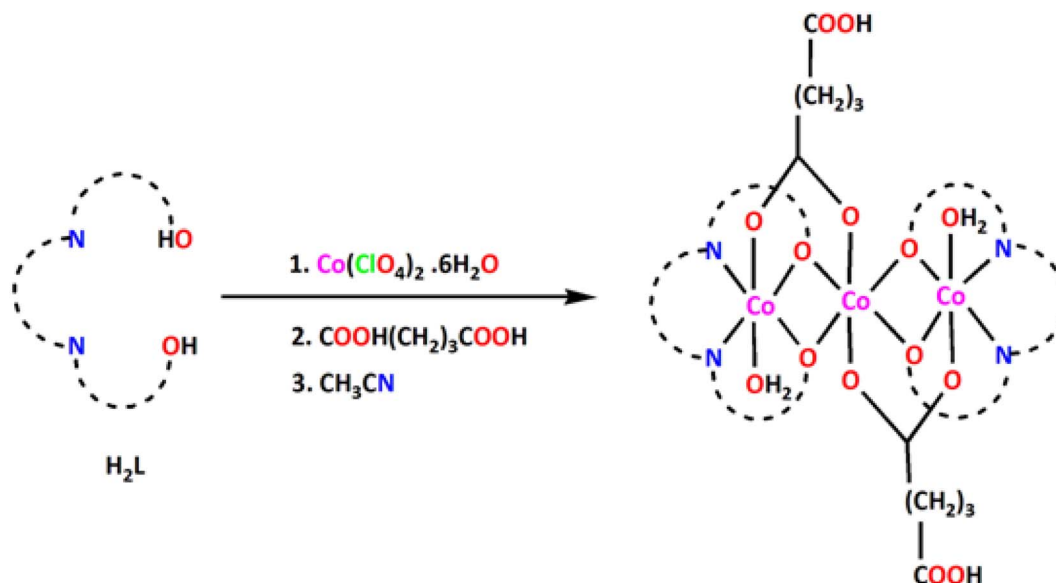
to explore the importance of aerial oxidation, the reactions were carried out under nitrogen atmosphere. In this case, we did not get any brown compound, but red coloured compound were isolated. Suitable single crystals of the compound could not be produced, but IR and mass spectral analysis and also elemental analysis indicates the formation of mononuclear cobalt(II) complex.

In the complex, the central cobalt center is assigned as cobalt(II) and both the terminal cobalt centers are assigned as cobalt(III), from BVS calculation and also from bond lengths data (Table 4). The central cobalt(II) is octahedral and is placed in O<sub>6</sub> donor environment, whereas the terminal cobalt centers are present in N<sub>2</sub>O<sub>4</sub> donor environment. As oxygen-donor ligands are having relatively weak crystal field, this may be a reason that +2 charges are favoured on this central cobalt. As cobalt(II) is high-spin with  $t_{2g}^5 e_g^2$  configuration, whereas cobalt(III) is essentially low-spin with  $t_{2g}^6$  electronic configuration, the oxidation of cobalt(II) to cobalt(III) involves the removal of one electron from  $e_g$  orbital and transfer of another electron from  $e_g$  to  $t_{2g}$ . Both these processes are favoured when the energy gap between  $t_{2g}$  and  $e_g$  is high. Thus, the oxidation of cobalt(II) is preferred in presence of stronger field of N-donor ligands, producing large energy gap between  $t_{2g}$  and  $e_g$ .

It may be noted here, the Schiff bases may be reduced with NaBH<sub>4</sub> to form the corresponding 'reduced Schiff base' ligands. These reduced Schiff bases may also be used to form similar mixed valence cobalt complexes. Recently we have reported the synthesis, structure and application of trinuclear mixed valence cobalt complexes of reduced Schiff bases containing different di-carboxylic acids as bridging co-ligands.<sup>100</sup>

### Description of structure of [Co<sup>II</sup>{(μ-L)(μ-Hglu)Co<sup>III</sup>(OH<sub>2</sub>)<sub>2</sub>}(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O

The complex consists of a linear, trinuclear, centrosymmetric, mixed valence cobalt(III)–cobalt(II)–cobalt(III) unit and



Scheme 2 The synthetic route to the complex.



Table 4 Result of BVS calculations of the complex

| Metal centre | <i>i</i> - <i>j</i> reported | <i>r</i> <sub>0</sub> | <i>i</i> - <i>j</i> of this complex | <i>r</i> <sub><i>ij</i></sub> | <i>S</i> <sub><i>ij</i></sub> | <i>Z</i> <sub><i>j</i></sub> |
|--------------|------------------------------|-----------------------|-------------------------------------|-------------------------------|-------------------------------|------------------------------|
| Co1          | O–Co <sup>2+</sup>           | 1.68                  | O(1)–Co(1)                          | 2.086                         | 0.336                         | 1.976                        |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(2)–Co(1)                          | 2.104                         | 0.316                         |                              |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(4)–Co(1)                          | 2.084                         | 0.336                         |                              |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(1a)–Co(1)                         | 2.086                         | 0.336                         |                              |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(2a)–Co(1)                         | 2.104                         | 0.316                         |                              |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(4a)–Co(1)                         | 2.084                         | 0.336                         |                              |
| Co2          | O–Co <sup>2+</sup>           | 1.68                  | O(1)–Co(2)                          | 1.923                         | 0.522                         | 3.51                         |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(2)–Co(2)                          | 1.912                         | 0.532                         |                              |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(3)–Co(2)                          | 1.888                         | 0.517                         |                              |
|              | O–Co <sup>2+</sup>           | 1.68                  | O(5)–Co(2)                          | 1.924                         | 0.522                         |                              |
|              | N–Co <sup>2+</sup>           | 1.80                  | N(1)–Co(2)                          | 1.929                         | 0.705                         |                              |
|              | N–Co <sup>2+</sup>           | 1.80                  | N(2)–Co(2)                          | 1.927                         | 0.712                         |                              |

crystallizes in triclinic space group,  $P\bar{1}$ . The central cobalt centre, Co(1), is in +II oxidation state, and the terminal cobalt centres, Co(2) and its symmetry related counterpart, Co(2)\*, are in +III oxidation states [symmetry transformation  $* = -x, 1 - y, -z$ ]. The perspective view of the complex including the selective atom labeling scheme is shown in Fig. 1. The oxidation states of cobalt(III) and cobalt(II) may be confirmed by charge balance considerations, inter-atomic cobalt-nitrogen and cobalt oxygen distances. In the complex, the central cobalt(II) centre, Co(1), is connected with the terminal cobalt(III) center, Co(2) and its centrosymmetric counterpart, Co(2)\* by two carboxylate and

four phenolate oxygen bridges forming bis{ $\mu$ -carboxylato- $\mu$ -phenonate} bridged cobalt(III)–cobalt(II)–cobalt(III) motifs, similar to the complexes reported in the literature.<sup>89,101</sup> It is interesting to note that two carboxylate bridges are *trans* in the centrosymmetric trimer, an arrangement observed in similar systems.<sup>89,101</sup>

The terminal cobalt center, Co(2), has a six-coordinate octahedral environment in which the equatorial plane is occupied by two phenolate oxygen atoms O(1) and O(2), and two imine nitrogen atoms, N(1) and N(2), of the di-Schiff base H<sub>2</sub>L. The axial positions are occupied by an oxygen atom, O(3), of

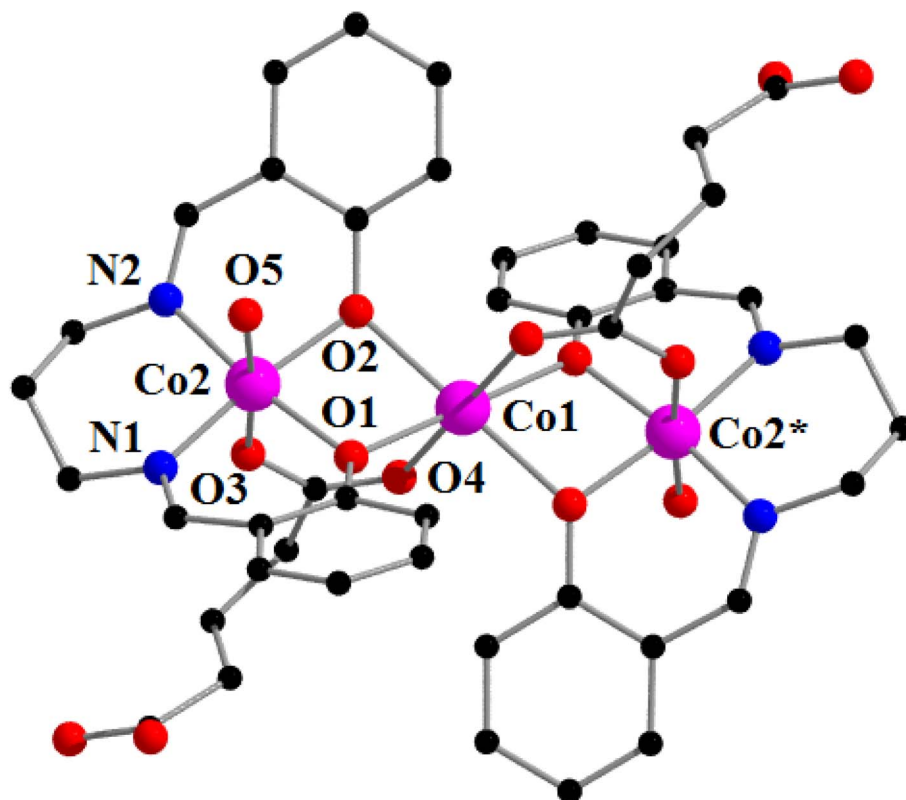


Fig. 1 Perspective view of the complex with selective atom-numbering Scheme. H atoms, perchlorate anions and lattice water molecules have been omitted for clarity. Symmetry transformation,  $* = -x, 1 - y, -z$ . Only one set of positions for the disordered  $-(CH_2)_3COOH$  group is shown.





Table 5 List of hydrogen bonding interactions studied in the complex

| Atoms involved<br>(D–H...A) | Distance<br>D–H (Å) | Distance<br>H...A (Å) | Distance<br>D...A (Å) | Angle<br>$\angle$ D–H...A (°) | Symmetry<br>transformation |
|-----------------------------|---------------------|-----------------------|-----------------------|-------------------------------|----------------------------|
| O(3W)–H(2W3)...O(24B)       | 0.82(8)             | 1.63(6)               | 2.27(1)               | 134(10)                       | —                          |
| O(5)–H(1W5)...O(2W)         | 0.85(3)             | 1.76(3)               | 2.606(4)              | 171(4)                        | —                          |
| O(5)–H(2W5)...O(1W)         | 0.83(4)             | 1.90(4)               | 2.731(6)              | 175(4)                        | —                          |
| O(1W)–H(2W1)...O(51)        | 0.84(7)             | 2.24(9)               | 2.906(7)              | 136(6)                        | —                          |
| O(2W)–H(2W2)...O(4)*        | 0.85(4)             | 1.94(4)               | 2.780(4)              | 174(4)                        | * = $-x, 1 - y, -z$        |

a bridging glutarate and a water molecule, O(5). Central Co(1), on the other hand, is coordinated by four phenolate oxygen atoms {O(1), O(2), and their symmetry related counter parts, O(1)\* and O(2)\*} [symmetry transformation \* =  $-x, 1 - y, -z$ ] and two oxygen atoms {O(4) and its symmetry related counterpart, O(4)\*} of a di-glutarate. Cobalt–cobalt bonding is not expected from the value of the Co(1)...Co(2) distance 3.076(3) Å.<sup>84,102,103</sup> The bridging angles,  $\angle$  Co(1)–O(1)–Co(2) = 100.1(1)<sup>0</sup> and  $\angle$  Co(1)–O(2)–Co(2) = 99.9(1)<sup>0</sup> indicate the non-collinear arrangement of the cobalt(III)–oxygen–cobalt(III) fragments.<sup>84,102,103</sup> The cobalt(III)–oxygen, cobalt(III)–oxygen and cobalt(III)–nitrogen distances (Table 2) are in the range 2.085(2)–2.103(2) Å, 1.889(2)–1.924(2) Å and 1.927(2)–1.928(2) Å, respectively, which are equivalent to those found in similar complexes reported in the literature.<sup>28,30,89,101</sup> There are four water molecules in the asymmetric unit, one coordinated O(5W) and three uncoordinated. All are involved in strong hydrogen bonds with details given in Table 5. These four water molecules form a network of H-bonds, as highlighted in Fig. 2, where the coordinated water molecule (O5) establishes two OH...O contacts with two different lattice water molecules (O1W and

O5W). One bridges O5 with the anion and the other bridges O5 with O4 (from the  $\mu$ -HGLu ligand).

### Theoretical study on supramolecular interaction

The DFT study is focused on one main aspect of the solid state structure of the complex, that is the H-bonding network highlighted in Fig. 2. That has been analyzed using the quantum theory of atoms in molecules. This method not only confirms the existence of the H-bonds, but also provides an estimation of the strength of the interaction *via* the value of the potential energy density at the bond CP that connect the H-atom to the O-atom. The QTAIM analysis is shown in Fig. 3. Each hydrogen bond is characterized by a Bond Critical Point (BCP, indicated by a small red sphere) and a bond path (depicted as an orange line) linking the hydrogen (from H<sub>2</sub>O) and oxygen atoms belonging to other water molecules, the  $\mu$ -HGLu ligand of the perchlorate anion. It is interesting to note that each perchlorate anion establishes two H-bonds, one with the nearby water molecule ( $-2.5$  kcal mol<sup>-1</sup>) and another one with one CH bond of the aromatic ring ( $-1.0$  kcal mol<sup>-1</sup>). In general, the H-bonds

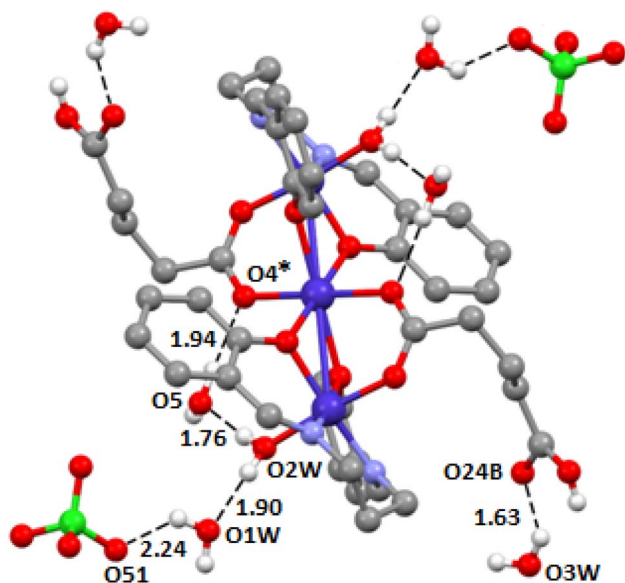


Fig. 2 Perspective view of hydrogen bonding network in the complex involving the coordinated and lattice water molecules as H-bond donor and acceptors. Only the relevant hydrogen atoms have been shown for clarity. Symmetry transformation, \* =  $-x, 1 - y, -z$ .

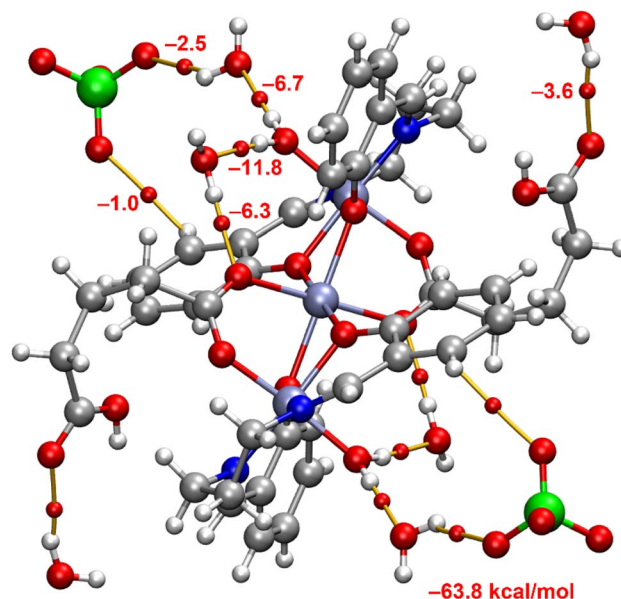


Fig. 3 QTAIM analysis (bond CPs in red and paths as orange lines) for the H-bonding network in the complex. Only H-bonding interactions are represented. The individual energies of the H-bonds were estimated using the equation  $E = 0.5 V$ , where  $V$  is the potential energy density at the BCP.



between water molecules are stronger than those involving the O-atoms of the anion. The strongest H-bond ( $-11.8 \text{ kcal mol}^{-1}$ ) correspond to the one that bridges the coordinated water molecule with the coordinated O-atom of the  $\mu$ -HGLu ligand [O(5)–H(1W5)···O(2W)] through a lattice water molecule. The formation energy of the H-bonding network is  $-63.8 \text{ kcal mol}^{-1}$ , which corresponds to the hydrogen bonding interactions shown in Fig. 3. This significant formation energy emphasizes the importance of the H-bonds in the solid state of the complex and also explain the incorporation of the co-crystallized water molecules.

### Hirshfeld surface analysis

Hirshfeld surface analysis is used to analyze the electronic distribution around the surface of a complex which helps in interpreting and visualizing the non-covalent interactions present in the crystal framework. Hirshfeld surfaces of the complex appeared over  $d_{\text{norm}}$  (range  $-0.1 \text{ \AA}$  to  $1.5 \text{ \AA}$ ), shape index and curvedness have been illustrated in Fig. S1.† Red spots on the  $d_{\text{norm}}$  Hirshfeld surfaces reveal the positions of strong contacts and interactions. The blue and white zone on the surfaces reveals weaker and longer contacts.

2D fingerprint plot of the complex show major interaction which is present in the form of H···H interaction, which constitutes of 45.7% of total surfaces of the complex. The proportion of C···H/H···C interaction and O···H/H···O interaction in the complex comprise of 14.4% and 37.6% of the Hirshfeld surface, respectively. The significant O···H interaction supports the complex to form a supramolecular 1D polymer. The intermolecular interactions appearing as distinct spikes in the 2D fingerprint plot is given in Fig. 4 (<https://www.sciencedirect.com/science/article/pii/S0277538722003916>).

### IR and electronic spectra

The bands in the range of  $1650\text{--}1550 \text{ cm}^{-1}$  are due to the presence of bridging carboxylate group.<sup>30,84,104</sup> In the IR spectrum of the complex, a distinct band appears around  $1600 \text{ cm}^{-1}$  and may be identified as stretching vibration of azomethine (C=N) group.<sup>30,105–107</sup> The IR spectrum also shows a weak band appearing in the range of  $2930\text{--}2880 \text{ cm}^{-1}$  due to stretching vibrations of alkyl C–H group.<sup>108–110</sup> The broad band observed around  $3250 \text{ cm}^{-1}$  in the IR spectrum is assigned to the O–H stretching vibration.<sup>103,109</sup> Two sharp bands around  $600 \text{ cm}^{-1}$

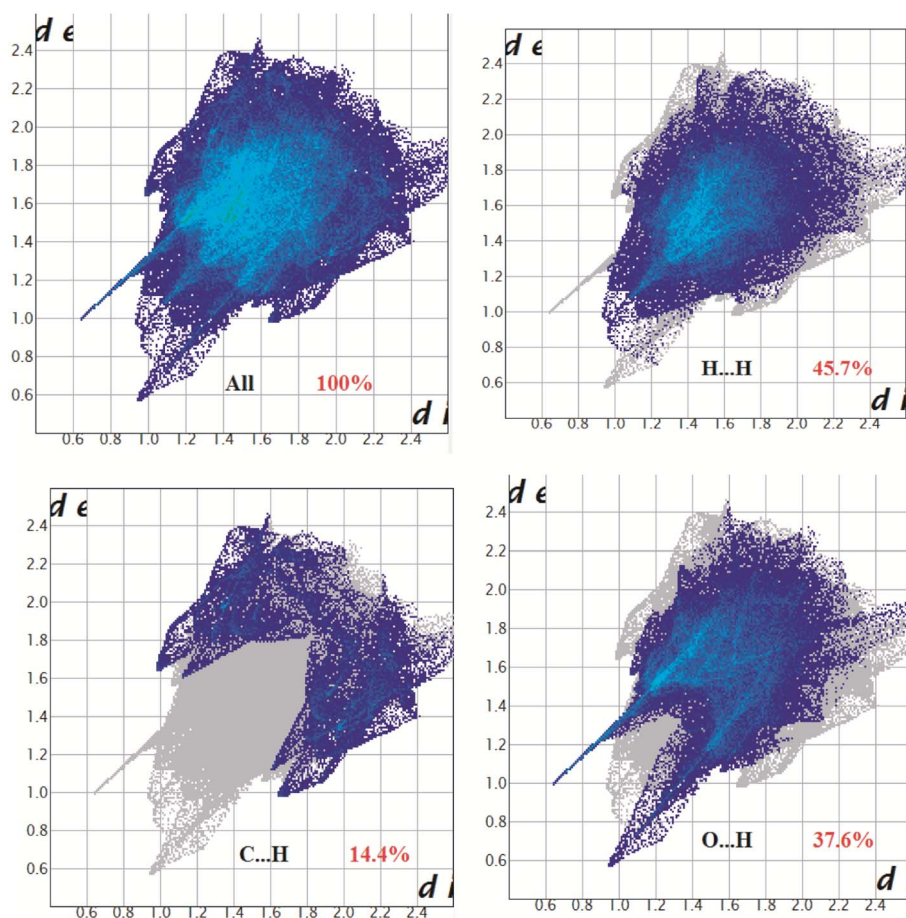


Fig. 4 Fingerprint plot of the complex: full and resolved into H···H, C···H/H···C and O···H/H···O contacts contributed to the total Hirshfeld surface area.

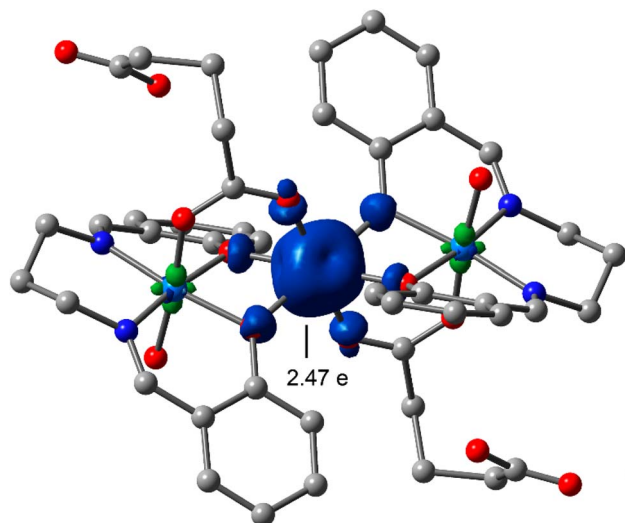


Fig. 5 Spin density plot of the cobalt(III/II/III) Schiff base complex reported in this work at the BP86-D3/def2-TZVP level of theory. The spin density at the Co(II) metal center is given.

and  $750\text{ cm}^{-1}$  are observed due to stretching of the Co–O and Co–N bonds, respectively.<sup>111–113</sup> The IR spectrum of the complex is given in Fig. S2.†

Electronic absorption spectrum of the complex in acetonitrile shows an intra-ligand  $\pi\text{--}\pi^*$  transitions at  $\sim 240\text{ nm}$ .<sup>114–116</sup> A strong ligand to metal charge transfer transition at  $\sim 430\text{ nm}$  has been observed which is characteristic of transition metal complexes with Schiff base ligands.<sup>84,110</sup> The band around  $585\text{ nm}$  may be assigned as one of the expected d–d transitions originated from cobalt(II).<sup>30,115,116</sup> The bands corresponding to the electronic transitions from cobalt(III) center are not observed as they are obscured by the transitions from cobalt(II) or by LMCT transitions.<sup>84,117,118</sup> The UV-vis spectrum of the complex is given in Fig. S3.†

### Magnetic moment

The effective magnetic moment at room temperature of the trinuclear complex is found to be 5.16 BM, which is indicative of the presence of only one high-spin Co(II) center in the molecule. The value is higher than the spin-only value for three unpaired electrons of high spin cobalt(II) with  $d^7$  electronic configuration. This may be due to orbital contribution of magnetic moment. The DFT study also supports that the spin density is localized on central cobalt with three unpaired electrons (2.47 e), as represented in Fig. 5, showing some spin delocalization toward the atoms directly bonded to the Co(II) atom.

## Conclusion

In conclusion, a new trinuclear, mixed valence, carboxylate bridged, cobalt(III)–cobalt(II)–cobalt(III) complex has been synthesized and characterized. Single crystal X-ray diffraction study has confirmed its structure. Moreover, the complex forms extended H-bonding networks using the Co(III)-coordinated

water ligands, the lattice water molecules and the carboxylic acid groups of the  $\mu\text{-HGLu}$  ligands. The energy associated to each H-bond has been estimated and the formation energy of the supramolecular H-bonding network calculated. It is very significant, revealing their strong influence in the crystal packing. We expect that the results reported herein may attract the interest of the crystal engineers and supramolecular chemists working with cobalt Schiff base complexes.

## Conflicts of interest

The authors declare no conflict of interest.

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