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# Isolation of a new anion, $[CdBr_4(C_7H_5O_2)]^3$ : Synthesis, single crystal X-ray structure determination and DFT calculations of $[Co(en)_3][CdBr_4(C_7H_5O_2)]\cdot H_2O$

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## ABSTRACT

A new anion  $[CdBr_4(C_7H_5O_2)]^{3-}$ , where  $C_7H_5O_2 =$  benzoate, has been isolated for the first time in the form of complex salt  $[Co(en)_3]$   $[CdBr_4(C_7H_5O_2)] \cdot H_2O(1)$ . This is the first example where Cd(II) centre is coordinated by both inorganic and organic ligands and existing as discrete unit. The complex salt is characterized by spectroscopic techniques and single crystal X-ray crystallography. The formation of complex salt is also supported by DFT calculations.

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Research in the field of organic-inorganic hybrid compounds is of great interest in chemistry and materials science because these compounds represent the combined properties of both organic and inorganic compounds within a single entity. This enables them to exhibit some interesting crystal structures and properties such as second-order nonlinear optical (NLO) response, magnetism, luminescence etc. [1–7]. Chemists often encounter the challenging task of design and later successful synthesis of such new materials. Although it is still a dream, but significant advances based upon analyses of large amount of experimental data have enabled chemists to understand the rationale of synthesis. A rational synthesis involves i) combination of reactants in proper stoichiometeric ratio and ii) choice of a suitable method (solgel, self assembly etc.). We have successfully exploited this strategy to synthesize novel halogeno/pseudohalogenomercurate(II) anions [Hg<sub>2</sub>  $(SCN)_7]^{3-}$  [8],  $[HgBr_5]^{3-}$  [9],  $[HgBr_4Cl]^{3-}$  [10] and polymeric halogenocadmate(II) anion  $[Cd_3Br_{10}(H_2O)_2]^{4-}$  [11] with the help of  $[Co(NH_3)_6]$ Cl<sub>3</sub>/Br<sub>3</sub>. During the successful isolation of [HgBr<sub>4</sub>Cl]<sup>3-</sup> anion, we have made an observation that it is possible to transfer bromide ions from first coordination sphere of  $[HgBr_5]^{3-}$  by using the proper stoichiometry of halide ions. Adhering to the above hypothesis, it was envisaged that it may be possible to synthesize new inorganic-organic hybrid materials in which one/few halide ions are replaced by appropriate organic ligands. In the present investigation, an attempt has been made to utilize complex salt [Co(en)<sub>3</sub>]Cl<sub>3</sub> for the synthesis of new anionic inorganic and organic hybrid material containing Cd(II) centre. Cadmium(II) is the metal of choice as its complexes have demonstrated both chemical and structural diversity [12,13], potential applications in catalysis, optical properties, [14–16] etc. while organic ligand selected was benzoate anion because of its significance in food and preservative industry [17,18].

Thus, we herein report our results of the reaction between [Co  $(en)_3$  Cl<sub>3</sub> with K<sub>2</sub> [CdBr<sub>4</sub>] and sodium benzoate. The reaction was carried out by two different methods. In first method,  $[Co(en)_3]Cl_3$  was reacted with K<sub>2</sub>CdBr<sub>4</sub> (formed by the reaction of KBr and CdBr<sub>2</sub> in aqueous medium) [19]. This resulted in the formation of crystalline yellow coloured product which was further reacted with sodium benzoate. In second method [Co(en)<sub>3</sub>]Cl<sub>3</sub>, K<sub>2</sub>[CdBr<sub>4</sub>] and sodium benzoate were reacted in a single pot without attempting to isolate the crystalline yellow coloured product as it was done in the first method. It was expected that reaction of [Co(en)<sub>3</sub>]Cl<sub>3</sub> with K<sub>2</sub>CdBr<sub>4</sub> would result in [Co(en)<sub>3</sub>][CdBr<sub>4</sub>Cl] and its reaction with sodium benzoate can result in a product where chloride may be replaced by benzoate ion. The products (crystals) obtained in both the cases were identical as indicated by melting point, elemental analyses and spectroscopic studies (FT-IR, NMR and UV/Visible). The authenticity of the same reaction product in both cases was confirmed by identical unit cell dimensions of their respective crystals obtained through single crystal X-ray crystallography. A schematic representation of the reaction procedure used is given in the Scheme 1.

Solubility product measurements at room temperature showed that complex salt **1** is less soluble in water as compared to tris(ethy-lenediammine)cobalt(III)chloride. The K<sub>sp</sub> values for **1** and [Co(en)<sub>3</sub>] Cl<sub>3</sub> are  $1.5 \times 10^{-3}$  and 195.3 respectively, indicating that the [Co (en)<sub>3</sub>]<sup>3+</sup> cation has more affinity for [CdBr<sub>4</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)]<sup>3-</sup> as compared to Cl<sup>-</sup>.

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#### Method 1

$$\begin{split} \mathbf{CdBr}_2 + 2\mathbf{KBr} & \xrightarrow{\mathsf{H}_2\mathsf{O}} \mathbf{K}_2[\mathbf{CdBr}_4] \\ & [\mathbf{Co(en)}_3]\mathbf{Cl}_3 + \mathbf{K}_2[\mathbf{CdBr}_4] & \xrightarrow{\mathsf{H}_2\mathsf{O}} \mathbf{Co(en)}_3][\mathbf{CdBr}_4 \cdot \mathbf{Cl}] + 2\mathbf{KCl} \\ & [\mathbf{Co(en)}_3][\mathbf{CdBr}_4 \cdot \mathbf{Cl}] + \mathbf{NaC}_7\mathbf{H}_5\mathbf{O}_2 \xrightarrow{\mathsf{H}_2\mathsf{O}} \mathbf{Co(en)}_3][\mathbf{CdBr}_4 \cdot \mathbf{C}_7\mathbf{H}_5\mathbf{O}_2] + \mathbf{NaCl} \end{split}$$

# Method 2

 $[Co(en)_3]Cl_3+K_2[CdBr_4] + NaC_7H_5O_2 \xrightarrow{H_2O} [Co(en)_3][CdBr_4,C_7H_5O_2] + NaCl+ 2KCl$ 

# where NaC<sub>2</sub>H<sub>5</sub>O<sub>2</sub> = sodium benzoate

Scheme 1. Schematic representation of reactions.

Conductance measurements were carried out at 25 °C in aqueous medium and a graph was plotted between  $\Lambda$  (molar conductance) and square root of concentration. The  $\Lambda_0$  value obtained was 536 S cm<sup>2</sup> mol<sup>-1</sup> for title complex salt which was closer to the values 561 and 531 S cm<sup>2</sup> mol<sup>-1</sup> reported for similar complex salt [Co(NH<sub>3</sub>)<sub>6</sub>][HgBr<sub>5</sub>] [9] and [Co(NH<sub>3</sub>)<sub>6</sub>][HgBr<sub>4</sub>Cl] [10], respectively.

The FT IR spectrum of complex salt was recorded in the region 400–4000 cm<sup>-1</sup>. The IR absorption bands at 3501, 3357, 1556, 1408, 850, 738, 461 cm<sup>-1</sup> were assigned to  $v_{as}(N-H)$ , v(O-H), v(C=C),  $v_s(N-H)$ ,  $r(NH_2)$ ,  $\delta(C-H)$ , v(Co-N) vibrations . To distinguish between the various bonding modes of carboxylate present in a compound, the magnitude of separation between  $v_{as}(COO^-)$  and  $v_s(COO^-)$ ,  $\Delta v$  (cm<sup>-1</sup>) is often used as diagnostic measure. The infrared absorption bands observed at 1585, 1323 cm<sup>-1</sup> were assigned to  $v_{as}(COO^-)$  and  $v_s(COO^-)$ , thus the value of  $\Delta v = 262$  cm<sup>-1</sup>. This indicated the presence of monodentate carboxylate group [20–22]. The FT IR spectrum of complex salt is shown in Fig. S1 in supporting information.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of complex salt **1** were recorded in D<sub>2</sub>O. In <sup>1</sup>H NMR, a doublet at 2.68 ppm was assigned to CH<sub>2</sub> protons of ethylenediamine groups of  $[Co(en)_3]^{3+}$ . Other three signals at 7.33, 7.41 and 7.72 ppm were assigned to the H3/5, H4 and H2/6 protons of benzoate ring. <sup>13</sup>C NMR spectrum showed the characteristic signal at 44.3 ppm for carbon atoms of ethylenediamine groups of complex cation. Signals at 135.6, 131.4, 128.8, 128.3, 175.81 ppm were assigned to carbon atoms C1, C2/6, C3/5, C4, C<sub>carboxylate</sub> of the coordinated benzoate ligand of complex anion  $[CdBr_4(C_7H_5O_2)]^{3-}$  [20,23,24].

UV/Visible spectrum of the title complex salt was recorded in water as a solvent. Two electronic transitions:  ${}^{1}A_{1g} \rightarrow T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  have been reported in literature for Co(III) containing complex salts around 470 and 340 nm, respectively [25]. For the title complex salt, the strong absorption maxima ( $\lambda_{max}$ ) were observed at 466 ( $\epsilon$ =89.9 mol<sup>-1</sup>L cm<sup>-1</sup>) and 338 ( $\epsilon$ =88.31 mol<sup>-1</sup>L cm<sup>-1</sup>) nm showing d-d

Table 1Crystal data and refinement details of complex salt 1.

Crystal data	
Chemical formula	$(CdBr_4C_7H_5O_2) \cdot (CoC_6H_{24}N_6) \cdot H_2O$
Mr	810.41
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	295
a, b, c (Å)	11.2045 (2), 11.7493 (2), 18.3147 (4)
V (Å <sup>3</sup> )	2411.04 (8)
Ζ	4
Radiation type	Μο Κα
$\mu$ (mm <sup>-1</sup> )	8.22
Crystal size (mm)	$0.50 \times 0.32 \times 0.29$
No. of measured, independent and	26232, 6995, 5712
observed $[I > 2\sigma(I)]$ reflections	
R <sub>int</sub>	0.055
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.115, 1.03
No. of reflections/no. of parameters	6995/253
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.96, -0.90

transitions typical for low spin Co(III) d<sup>6</sup> octahedral complexes while a shoulder observed at 221 nm was due the aromatic ring of benzoate.

Single crystal X-ray structure determination was undertaken to unambiguously establish the structure [26–31]. The crystal data and refinement parameters are reported in Table 1. The asymmetric unit of **1** consists of a tris(ethylenediamine)cobalt(III) complex cation, counter-anion benzoatotetrabromo cadmate(II) and a water molecule as solvent of crystallization. The ORTEPIII diagram [32] of complex salt is shown in Fig. 1. The coordination geometry around the Co(III) centre is slightly distorted octahedral mainly due to the ethylenediamine bite. The selected bond lengths and bond angles are reported in Table S1 in supplementary information. In the anion,  $[CdBr_4(C_7H_5O_2)]^{3-}$  the coordination around Cd(II) centre is five and to the best of our knowledge  $[CdBr_5]^{3-}$  is surprisingly unknown  $([CdBr_4]^{2-}$  and  $[CdBr_6]^{4-}$  are well documented in the literature), how-ever analogous  $[CdCl_5]^{3-}$  exists [33]. The Cd(II) metal ion is bound to four bromide and one oxygen of the benzoate moiety, leading to a distorted square pyramidal geometry, in which the Cd(II) metal ion is located 0.38 Å above the basal mean plane. The Br3 atom is in apical position, and the angle formed by the Cd–Br3 line and normal to (Br1, Br2, Br4, O2)-least-squares plane measures 176.08(3)°. In an effort to classify the existing cadmium-benzoate complexes, a CSD search [34] has been done on penta- and hexa-coordinated cadmium(II) complexes containing the benzoate fragment (or its derivatives). Out of 55 pentacoordinated complexes retrieved, in 18 cases the ligand acts as a bidentate towards the same metal atom and the Cd-O bond distances vary in the range of 2.21–2.67 Å. In the present structure, however, the Cd – O1 bond distance is 2.725(5) Å which is longer than the range observed in CSD search. This may be due to the monodentate nature of the benzoate anion which is unique in the present structure. In the remaining 37 structures, the carboxylate group bridges two metal centres.

In the 298 structures (CSD) of hexacoordinated Cd(II) complexes both the oxygen atoms are bound to Cd with bond lengths in the range of 2.21–2.78 Å while 174 entries have been found with the benzoate ligand classified as monodentate. Here, the Cd–O bond distances range from 2.14 to 2.56 Å. A further search of structures containing the  $[CdX_5]^{3-}$  anion (X = any halogen) yielded only one Hit, FOWLEJ [35] where the coordination geometry around the metal ion is trigonal bipyramidal (as shown in Fig. 2).

DFT calculations have been performed on the Cd(II) complex anion [36–40], starting from the geometry found in the crystal. These calculations are of particular interest in view of the different behaviour displayed by the complex when considered *in vacuum* and in a simulated solvent (water). The optimization process in gas phase failed, as it was not converging after 80 cycles; it is however worth mentioning that the benzoate anion shows a tendency to dissociate from the CdBr<sub>4</sub> fragment, in the last cycle the carboxylate oxygen atoms became 5 Å apart from Cd atom. The same results have been obtained when optimization was started from a hexacoordinated Cd atom, in which both oxygens were bound to the central metal. On the contrary, in simulated water the complex did not



Fig. 1. ORTEPIII view and atom numbering scheme for complex salt 1. Thermal ellipsoids are drawn at the 40% probability level. Average bond distances are Co-N=1.966(6), Cd-Br=2.7045(8), Cd-O2=2.309(5), C-O=1.248(8).

dissociate and assumed the geometry as shown in Fig. 3 (calculated coordinates for the molecule are given in Table S2 in supporting information). Here the two carboxylate oxygens were almost equidistant from the central atom, and the coordination can be described as highly distorted octahedral. The Cd–Br distances were longer than those found in the crystal, being in the range of 2.77–2.87 Å, but in line with the values found in the only structure containing the  $[CdBr_6]^{4-}$  ion [41] which vary from 2.745 to 2.814 Å. Therefore, it may be hypothesized that what found in the crystal is a snapshot of an incipient association process of the carboxylate oxygen atoms to the metal centre which however has to compete with the presence

of a water molecules forming hydrogen bonds with both the benzoate oxygen atoms.

The packing architecture is quite complicated, in view of the large number of available hydrogen-bond donors and acceptors. All N–H groups of the ethylenediamine moieties are involved in hydrogen bonds, whose structural parameters are reported in Table S3 in supporting information. The strongest hydrogen bonds are however made by the free water molecule, which acts as a donor towards O1 and O2 atoms of the benzoate anion and accepts a H–bond from N5, as shown in Fig. 4(a), linking the alternately placed cations and anions along the *b* direction. Besides these bonds, the crystal architecture is made more robust by several weaker C–H…O/Br interactions.





Fig. 2. Coordination around the Cd atom in FOWLEJ.

Fig. 3. Optimized geometry in simulated solvent (water). Cd-O distances (Å) are shown.



Fig. 4. (a) Molecular arrangement around the water molecule which is acting as linker between anion-anion and cation-anion. (b) Cell contents (viewed along *a* axis). Polyhedra around the Co and Cd atoms are shown in blue and grey, respectively.

The overall packing pattern is shown in Fig. 4(b), where the complexes are represented by their coordination polyhedra.

Thus, the synthesis of new a anion  $[CdBr_4(C_7H_5O_2)]^{3-}$  has been described which is isolated in the form of complex salt  $[Co(en)_3][CdBr_4(C_7H_5O_2)]\cdot H_2O$  for the first time. To the best of our knowledge, this is the first structural report of five coordinated Cd(II) metal ion having organic (benzoate) and inorganic (bromide) ligands attached to it and exiting as a discrete anion. The formation of this new anion is facilitated by a cation  $[Co(en)_3]^{3+}$  which can involve in second-sphere hydrogen bonding interactions i.e. N–H...O, C–H...O/Br besides electrostatic forces of attraction.

## Appendix A. Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre, CCDC No. CCDC 816619, comprises the final atomic coordinates from all atoms, thermal parameters, and a complete listing of bond distances and angles. Copies of this information may be obtained free of charge on application to The Director, 12 Union Road, Cambridge, CB2, 2EZ, UK, fax: +44 1223 336 033, e-mail: data\_request@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk. The supplementary material also contains Fig. S1, Tables S1–3. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.10.020.

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(KBr pellet): 35.01(m), 3357(m), 3194(b,s), 1585(s), 1556(s), 1408(s), 1323(m), 1159(s), 1056(s), 850(s), 738(s), 494(w), 461(w) cm^{-1}. UV/Vis (solution):  $\lambda_{max}$  466 nm ( $\epsilon$  = 89.94 L mol<sup>-1</sup> cm<sup>-1</sup>), 338 nm ( $\epsilon$  = 88.31 L mol<sup>-1</sup> cm<sup>-1</sup>)

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