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A new binuclear Cr(III) citrate anion: Synthesis, characterization and crystal structure of $[Cr(CO(NH_2)_2)_6]_2[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]_3$

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ABSTRACT

The new anion $[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]^{2-}$ has been isolated in the complex $[Cr(CO(NH_2)_2)_6]_2[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]_3$. The crystals of this complex were obtained by a one-pot synthetic method using 1:1 molar ratio of hexaureachromium(III) chloride and trisodium citrate in aqueous medium. It was characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction analysis. The compound crystallizes in space group $R\bar{3}$ of the trigonal system with three formula units in a cell of dimensions $a=b=24.7461(4)$ Å, $c=13.7204(3)$ Å and $\gamma=120°$. The crystal structure comprises the columns consisting of $[Cr(CO(NH_2)_2)_6]^{3+}$ cations surrounded by a cylinder of complex anions, $[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]^{2-}$ which are packed in a honeycomb-like manner. This supramolecular architecture is formed and stabilized by inter- and intramolecular N–H··O hydrogen bonds.

Chromium(III) complexes has significant role in catalytical [1], electroplating [2] and photochemical reactions [3]. Biologically, chromium(III) is an essential micronutrient required for proper carbohydrate and lipid metabolism in mammals [4] and protein precipitation processes [5]. It is an active ingredient of the glucose tolerance factor (GTF) and its deficiency leads to moderate diabetes mellitus [6]. Supplementation of a GTF-deficient diet with chromium (in the form of hexaureachromium(III) chloride) results in a significant increase of intravenous glucose tolerance [7]. As hexaureachromium(III) chloride can form number of complexes [8–15] by reacting with various metal salts, we envisaged that octahedral hexaureachromium(III) cation should provide two triangular urea faces with twenty four –NH bonds (from twelve $-NH_2$ groups) that can act as potential hydrogen bond donors. The biologically important anion, citrate was selected because the oxygen atoms of three carboxylate groups act as hydrogen bond acceptors and hydroxyl groups act as hydrogen bond donor. Including all the probabilities in the solid state, these two ions should form an intricate network of hydrogen bonds and electrostatic force of attractions stabilizing the entire lattice. Understanding of such network interactions of judicially chosen cations and anions would be rewarding as it can provide means of constructing intricate and novel molecular entities based on second-sphere coordination.

Expecting such network we have reacted hexaureachromium(III) chloride with a trisodium citrate in 1:1 molar ratio in aqueous medium with the expectation of hexaureachromium(III) citrate. The grayish green product was obtained after two days which is insoluble in water, DMSO and any other commonly used organic solvents (like $(CH_3)_2CO$, EtOH, $CHCl_3$ etc.). The elemental analysis was not in the agreement with the expected product i.e., $[Cr(CO(NH_2)_2)_6](C_6H_5O_7)$.

Infrared spectrum of the complex was recorded in KBr pellets and it shows typical absorption bands for coordinated urea ligands which are comparable with hexaureachromium(III) chloride [16]. In anion, $[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]^{2-}$ the frequencies of the observed carbonyl vibrations were shifted to lower values in comparison to the corresponding vibrations in free citrate ion and citric acid, indicating changes in the vibrational status of the citrate ligand upon binding to Cr(III) [17,18]. In the title complex, sharp peaks for asymmetric and symmetric COO^- stretch were observed at 1624 and 1419 cm^{-1} respectively. The difference between ν_{as} and ν_s i.e., $\Delta\nu=(\nu_{as}(COO^-)-\nu_s(COO^-))$ is 205 cm^{-1}, which is greater than 200 cm^{-1} indicating that the carboxylate groups of the citrate ligand are either free or coordinated to Cr(III) in a monodentate fashion [17,18]. The observation is consistent with X-ray crystal structure of title complex showing that the carboxylate groups of citrate ion are bonded in monodentate fashion.

Single crystal X-ray structure determination of the title complex revealed the presence of two symmetry independent complex cations, $[Cr(CO(NH_2)_2)_6]^{3+}$ and dimeric complex anions, $[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]^{2-}$ shown in Fig. 1. Coordination bond lengths are given in caption of Fig. 1. The remaining bond lengths and angles are available in supporting material. The primary coordination sphere of Cr1 and Cr2 atoms within cations is composed of six urea molecules and each urea molecule is coordinated terminally through O atom forming approximately octahedral geometry. Cr1 and Cr2 atoms lie on 3-fold rotoinversion axis. The Cr–O bond distances are in range 1.958 (2) and 1.966 (3) Å for Cr1 and Cr2 respectively, which is in

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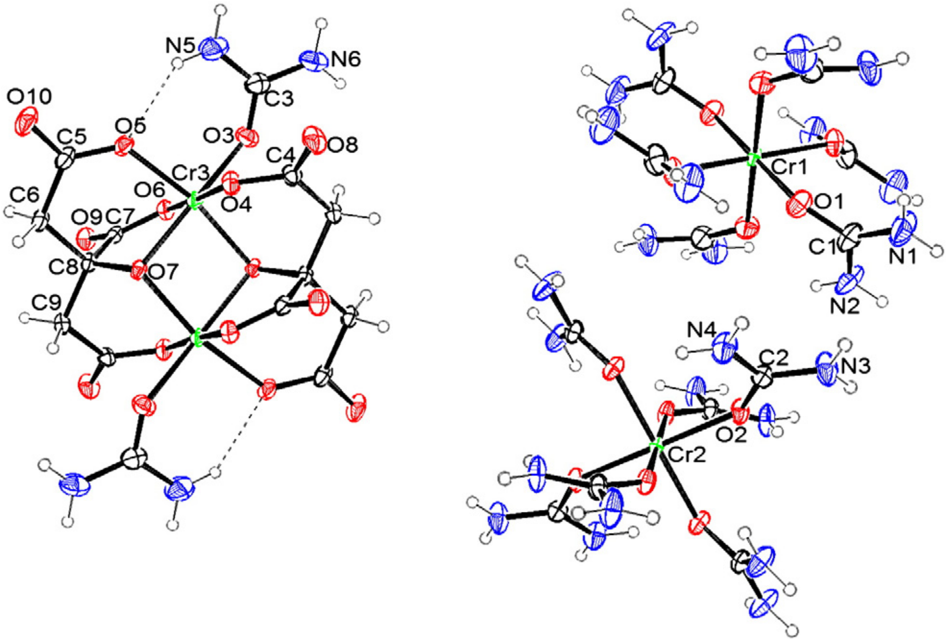

Fig. 1. Structure of $[Cr(CO(NH_2)_2)_6]_2[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]_3$ with the atom-labeling scheme of the asymmetric unit. Thermal ellipsoids are drawn by ORTEP and represent 25% probability surfaces. Coordination bond lengths (Å): Cr1 – O1 1.965 (3), Cr2 – O2 1.958 (2), Cr3 – O3 1.987 (3), Cr3 – O4 1.969 (2), Cr3 – O5 1.978 (2), Cr3 – O6 1.963 (2), Cr3 – O7 1.981 (2), Cr3 – O7$_{(1-x,y,z)}$ 1.979 (2).

agreement with those found in the other hexaureachromium(III) complexes [13,14,19]. The main difference between both symmetry independent cations is in their conformation which is reflected in different Cr – O – C – N torsion angles which are ±54.2, ±127.5 (in cation containing Cr1) and ±9.4, ±171.2 (in cation containing Cr2), respectively. Additionally, bond angles around Cr1 deviate more from ideal 90°/180° in comparison with those in Cr2 indicating larger distortion of ideal octahedral coordination. Difference in the conformation of both symmetry independent cations can also be seen in Fig. 2.

The counterion of the hexaureachromium(III) complex is a new anion di-μ-citrato(– O –)-di(ureachromate(III)). The complex anions are centrosymmetric dimers with two bridging citrato ligands and two terminal urea ligands. Both Cr(III) atoms are octahedrally coordinated by six O atoms. One O atom belongs to carbonyl group of urea bonded terminally in monodentate mode. Three O atoms are from the first bridging citrato ligand and two from another bridging citrato ligand. As shown in Fig. 1, each citrate ligand is bonded to two Cr(III) through four coordination sites: three from carboxylate groups and one from oxo group. Two of three carboxylate groups of each citrate ligand are coordinated in monodentate manner (Cr – OCO) to one Cr(III) metal ion and the third carboxylate group is bonded in the same way to another Cr(III) central ion. The oxo group (in both citrate ligands) is coordinated to both Cr(III) central atoms in bridging mode (Cr – O – Cr). The Cr – O distances are in range 1.963 (2)–1.987(3) Å. On the other hand there are known similar Co(II) and Fe(III) complex anions with analogous citrato bonding, where instead of terminal urea there is water coordinated. In these structures the counterions are different heteroaromatic cations [20]. Fig. 3 presents crystal packing of title compound. $[Cr(CO(NH_2)_2)_6]^{3+}$ cations are stacked one upon another in [001] direction (along inversion triad), with regular alternation of cations containing Cr1 and Cr2 atom. This way they form columns running parallel *c* axis. Each column is surrounded by a “cylinder” consisting of complex anions, $[Cr_2(CO(NH_2)_2)_2(C_6H_4O_7)_2]^{2-}$. Such columns are packed in a distinctive honeycomb-like manner. The complex anions form the walls of the honeycomb and the cations behave as a honey. This supramolecular architecture is formed and stabilized by intermolecular hydrogen bonds between amino groups of $[Cr(CO(NH_2)_2)_6]^{3+}$ cations and oxygen atoms from citrate ligands of complex anions. The N atoms of urea amino groups are also donors of intramolecular hydrogen bonds within cations and anions. In both symmetry independent cations the one N atom of urea ligand which is a donor of H bond to O atom of carbonyl group of neighboring urea ligand from the same coordination cation. In the coordination anion each urea ligand is through N5 atom a donor of H bond to carboxylic O5 atom of citrate ligand. The H-bonding parameters are given in Table 1. The comparison between intermolecular H-bonds donated by N atoms from Cr1 containing cation with those from Cr2 containing cation shows that these two cations have different second coordination sphere. Each urea from Cr1 containing cation is involved in only one intermolecular H bond and one intramolecular H-bond: N1 atom is a donor of intermolecular H bond accepted by uncoordinated carboxylato O9 atom from citrato ligand. N2 atom is a donor of intramolecular H bond. So, two H atoms per urea molecules are not involved in classic hydrogen bonding. On the other all H atoms in urea from Cr2 containing cation are involved in N – H···O hydrogen bonding (each urea in four of them). N3 atom is a donor of two intermolecular H bonds and N4 of one intermolecular and one intramolecular H-bond. The acceptors of all three intermolecular H bonds are carboxylate O atoms (O8, 010 and O4) from citrato ligand of complex anion. O8 and O10 are uncoordinated, while O4 is coordinated to Cr3 atom. In spite of both Cr1 and Cr2 containing cations are encircled by cylinder of complex anions but their environment is not the same. They are surrounded by and H-bonded to different atoms from complex anion. Such differences in this second coordination sphere are connected with the differences in the conformation of Cr1 and Cr2 containing cations. They adopt such conformation that intermolecular interactions, especially H-bonding, stabilize the structure as much as possible.

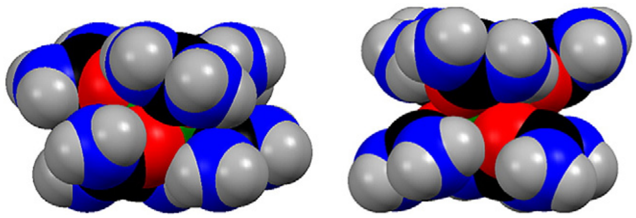

Fig. 2. Space filling representation of Cr1 (left) and Cr2 (right) containing complex cations.