Synthesis, spectroscopic and X-ray structure characterization of ethylenediammonium chromate and ethylenediammonium dichromate

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The reaction of ethylenediammonium chloride (enH₂)Cl₂ with potassium chromate or dichromate in a 1:1 molar ratio results in the formation of the title complexes ethylenediammonium chromate (enH₂)[CrO₄] I and ethylenediammonium dichromate (enH₂)[Cr₂O₇] II in good yields. The two complexes have been characterized by IR, UV-Vis, 1H NMR spectroscopy and metal analysis and their structures have been determined by single crystal X-ray crystallography. Ethylenediammonium chromate I crystallizes in the orthorhombic space group P2₁2₁2₁ (IT-Nr. :19) with the unit cell dimensions: a = 6.656(1) Å, b = 8.869(1) Å, c = 11.831(2) Å, V = 698.4(2) Å³, Z = 4. The structure of I consists of tetrahedral tetraoxochromate dimians, with the Cr at the center of the tetrahedron. Ethylenediammonium dichromate II crystallizes in the monoclinic space group C2/c (IT-Nr.:15) with the unit cell dimensions: a = 13.464(2) Å, b = 7.591(1) Å, c = 8.639(1) Å, β=108.97(1)°, V = 857.0(2) Å³, Z = 4. In both the compounds, short H-bonding contacts are observed between the oxygen atoms bound to the Cr containing diamine and the H attached to the N atom of the organic diacation.

Chromium(VI) based reagents are an important class of compounds, which are extensively used in organic syntheses to effect a variety of synthetic transformations. The commonly used Cr(VI) reagents are chromium trioxide (CrO₃) in combination with a variety of organic compounds like acetic acid or acetic anhydride or pyridine etc., a mixture of sodium dichromate and concentrated sulphuric acid and pyridinium chlorochromate. In the last two decades, chromium(VI) reagents in combination with amines have been widely used for the oxidation of alcohols to the corresponding carbonyl compounds. It has been shown that the nature of the amine determines the oxidizing power of the chromate ion and this is inversely related to the donor strength of the associated amine ligand. Tetramethylethylenediammonium dichromate and piperazinium dichromate, which contain tetramethylethylenediamine and the cyclic diamine piperazine in their diprotonated form have been recently introduced as reagents in organic syntheses as mild oxidants.

The [CrO₄]⁻ tetrahedron can be used as an acentric building block to create non-centrosymmetric materials. Based on this strategy, Poeppelmeier and coworkers have reported the synthesis of novel dichromates having formula [M(py)$_2$]Cr$_2$O$_7$ (M=Cu, Zn or Cd). Of these, the Zn and Cu dichromates exhibit interesting structural features like neutral non-intersecting one-dimensional chains of M(py)$_2$Cr-O- and nonlinear optical properties. Although a number of chromates and dichromates containing inorganic cations have been structurally characterised, relatively few structures of Cr(VI) compounds containing organic cations have been determined. An important aspect of the reported structures of the organic salts of Cr(VI) compounds is the identification of an extended H-bonding network in these systems. In view of the importance of organic salts of chromate and dichromate in synthetic organic chemistry, and also their emerging importance as useful materials, it is desirable to develop new synthetic methodologies for the preparation of such salts and also to determine the three dimensional structures. Hence, the study of Cr(VI) compounds are of current interest. As part of an ongoing programme aimed at the synthesis of Mo/W-S compounds containing organic dications, the structures of (enH₂)[M'S₄] (en-ethylenediamine M' = Mo or W) have already been reported by us recently. We have extended this chemistry to the corresponding oxochromates and developed a convenient synthetic route for the preparation of the ethylenediammonium salts of chromate and dichromate. The results of these investigations are described in this paper.
Materials and Methods

Solvents and reagents were used as obtained from commercial sources in this investigation. Infrared spectra in the 4000-400 cm\(^{-1}\) region were recorded on a Shimadzu (Model 8101A) FTIR instrument. The samples were pressed as KBr diluted pellets in the solid state and the infrared signals referenced to polystyrene bands. UV-Vis spectra were recorded on a Shimadzu UV-1601 instrument using matched quartz cells. The \(^1\)H NMR spectra of (enH\(_2\))CrO\(_4\)\(\cdot\)H\(_2\)O and (enH\(_2\))\(\frac{1}{2}\)Cr\(_2\)O\(_7\) were recorded in DMSO-\(d_6\) and D\(_2\)O on a Bruker 300 MHz instrument at the National Institute of Oceanography (NIO), Goa. Chromium analyses were performed gravimetrically following a standard procedure\(^{22}\). Single crystal X-ray structure determination was performed on a AED2 four-circle diffractometer.

Preparation of ethylenediammonium chromate 1

K\(_2\)[CrO\(_4\)] (1.94 g, 0.01 mol) was dissolved in water (20 ml) and (enH\(_2\))Cl\(_2\) (1.33 g, 0.01 mol) in water (5 ml) was slowly added at room temperature. The yellow coloured solution thus obtained was filtered and kept in the refrigerator for crystallisation. After 2 days yellow block-like crystals were obtained. The crystalline product was filtered and washed with ice-cold water (~5 ml) and air-dried. Yield (54\%). IR Data: 2971-2365(br), 1607 (m), 1526 (m), 1466 (m), 1412 (w), 1327 (w), 1256 (w), 1098 (m), 1067 (m), 1021 (s), 924 (s), 801 (br), 777 (m) cm\(^{-1}\). UV-Vis. Data: 270 nm (\(\varepsilon=2500\)), 270 nm (\(\varepsilon=2480\))

Anal. Found (calcd.): Cr 29.1% (29.2%).

Preparation of ethylenediammonium dichromate 2

K\(_2\)[Cr\(_2\)O\(_7\)] (2.94 g, 0.01 mol) was dissolved in water (25 ml) and (enH\(_2\))Cl\(_2\) (1.33 g, 0.01 mol) in water (10 ml) was slowly added at room temperature. The orange coloured solution thus obtained was filtered and kept aside for crystallisation. After 2-3 days orange crystalline blocks were obtained. The crystalline product was filtered and washed with ice-cold water (~10 ml) and air-dried. Yield (65\%). IR Data: 3063-2512 (br), 1615 (m), 1556 (m), 1501 (m), 1470 (m), 1360 (m), 1333 (w), 1065 (m), 1022 (m), 930 (s), 878 (m), 787 (w) cm\(^{-1}\). UV-Vis. data: 353 nm (\(\varepsilon=2770\)), 260 nm (\(\varepsilon=3700\))

Anal. Found (calcd.): Cr 37.3% (37.4%).

Results and Discussion

The reaction of an aqueous (enH\(_2\))Cl\(_2\) solution with K\(_2\)[CrO\(_4\)] or K\(_2\)[Cr\(_2\)O\(_7\)] in a 1:1 mole ratio readily affords the title compounds in good yields and the product formation can be represented as shown below:

\[
\begin{align*}
K_2[CrO_4] + (enH_2)Cl_2 &\rightarrow (enH_2)[CrO_4] + 2 KC1 \\
K_2[Cr_2O_7] + (enH_2)Cl_2 &\rightarrow (enH_2)[Cr_2O_7] + 2 KC1
\end{align*}
\]

where ‘en’ stands for ethylenediamine

The more soluble KCl remains in solution and the organic chromates crystallise out from the reaction mixture. The reaction of ammonium chromate with ‘en’ also leads to the formation of ethylenediammonium chromate 1. In this reaction the weaker base ammonia is replaced by the stronger base en resulting in product formation. This type of base promoted cation exchange reaction has been used earlier by the authors for the preparation of ethylenediammonium tetrafluoroborate\(^{22}\) and tetrathiotungstate\(^{23}\).

An attempted synthesis of fluoropolychromate\(^{18}\) by reacting CrO\(_3\), ‘en’ and HF has instead resulted in the formation of 2. The use of HF in a solvothermal reaction containing MO (M=Cu, Zn or Cd), (pyH\(_2\))[Cr\(_2\)O\(_7\)], (py=pyridine), py and H\(_2\)O in an autoclave at 150°C for 24 h has resulted in the formation of the M(py)\(_2\)Cr\(_2\)O\(_7\) dichromate complex. These observations clearly indicate that in acidic media the only products that can be obtained are the dichromates. It has been recently reported that 1,4-butanedithiammonium chromate\(^{23}\) can be obtained by reacting CrO\(_3\) with the organic diamin e in water.

It appears that in neutral or basic conditions the preferred product is the chromate, while under acidic conditions, dichromates are the preferred products. However, the use of (enH\(_2\))Cl\(_2\) can readily afford either the chromate or the dichromate by a simple cation exchange reaction. Further, these reactions do not involve the use of any acid like HF or a free organic base. Hence, the present synthesis can be considered as a convenient and rational synthesis for the preparation of organic salts of oxochromates.

A combination of IR, UV-vis, NMR and elemental analysis techniques has been employed to characterize the title complexes 1 and 2. The solid state infrared spectra of both the complexes 1 and 2 exhibit several signals indicating the presence of the organic dication. The broad absorption signal at 2970-2365 cm\(^{-1}\) in 1 can be assigned to C-H and N-H stretching vibrations.
This signal is quite broad compared to the signal observed in other ethylenediammonium salts like (enH₂)[MoS₄]²² and occurs at lower energies. This feature is indicative of H-bonding interactions and the broadness of the signal indicates that the H-bonding interactions are stronger in the tetraoxochromate. Shorter H-bonding contacts of the order of 2.0 Å between the H atoms and the O atoms have been observed (vide infra) in this compound. The broad signal observed at 3063-2512 cm⁻¹ in 2 can be assigned to the N-H and C-H stretching vibrations. The strong signals observed at 924 and 835 cm⁻¹ in 1 can be assigned to Cr-O vibrations while all the other signals can be attributed to the organic ethylenediammonium counter cation. The bands observed at 930 and 878 cm⁻¹ for the dichromate complex 2 can be assigned to the asymmetric and symmetric Cr-O stretching vibrations and are in good agreement with the reported values of the same compound prepared in a HF medium. The electronic spectrum of 1 in H₂O exhibits bands at 373, 270 nm while the dichromate complex 2 absorbs at 353 and 260 nm. These bands can be assigned to the charge transfer transitions of the oxochromates.

The high field ¹H NMR spectra of complexes 1 and 2 are very similar. For the sake of comparison the NMR spectra of two other ethylenediammonium salts were also recorded. Both 1 and 2 exhibit sharp singlet resonances in D₂O at δ 3.16 and δ 3.24 ppm, which can be readily assigned to the two methylene groups. The signal due to the ammonium protons are not observed in both cases in D₂O, which can be attributed to the rapid exchange of these protons. However, in DMSO-d₆, the resonances due to both types of protons are observable. One of these signals is broad and the addition of D₂O results in the disappearance of this broad signal. The broad signal is assigned to the resonance absorption of the protons bound to N. The resonance due to the N-H protons in 1 is observed at δ 3.43 ppm while the signal for the protons bound to N in 2 occurs at δ 7.78 ppm. Interestingly in two other (enH₂)²⁺ salts the absorption of the proton bound to N is observed at around δ 8 ppm. The reason for the upfield shifting of the –NH₃ signal in 1 is not very clear. A magic angle spinning experiment (solid state NMR) of 1 will clarify the picture. Thus, the NMR spectral data conclusively prove the presence of the organic cation in the title complexes.

Intensity data for the title complexes 1 and 2 were collected on an AED2 four-circle diffractometer using graphite monochromated Mo-Kα radiation. Lattice parameters were obtained by the least-squares refinement of 92 reflections for 1 and 139 reflections for 2. The intensities of four standard reflections were monitored periodically throughout the course of data collection and no significant decay was detected. The structure was solved with direct methods using SHELXS-97 and the refinement was done against F² using SHELXL-97. Anisotropic displacements were used for C, N, O and Cr while the H atoms were positioned in idealised geometry and refined using the riding model with fixed isotropic displacement parameters. For compound 1 the absolute structure was determined and is in agreement with the selected setting [Flack-x-parameter: 0.009(18)]. In agreement with this, refinement of the inverse structure leads to significant poorer reliability factors (R1 for all 1977 F > 4σ(Fo) = 0.0303; WR2 for all unique data: 0.0849). The technical details of data acquisition and some selected refinement results are summarised in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for 1 and 2 are presented in Table 2.

**Crystal structure of (enH₂)[CrO₄] I**

Ethylenediammonium chromate 1 crystallizes in the orthorhombic space group P₂₁2₁2₁ and is isostructural with the previously reported ethylenediammonium salts like (enH₂)[MS₄] (M = Mo²², W²²). The substitution of Mo or W by Cr and the substitution of S by O in 1 has resulted in a decrease in the unit cell dimensions a, b, c and a consequent reduction in the unit volume. The unit cell volumes of the Mo and W complexes are 938.7 (9) and 952.75 (9) Å³ respectively. The structure of complex 1 can be described as consisting of tetrahedral dinegative tetraoxochromate anions hydrogen bonded to the ethylenediammonium dications. The ellipsoid plot of the [CrO₄]²⁻ anion in 1 is shown in Fig 1 and selected bond lengths and bond angles for 1 are listed in Table 3. The Cr(VI) ion is tetracoordinated by four oxygen atoms. The tetrahedral environment is only slightly distorted as evidenced by the O-Cr-O bond angles with values ranging from 107.71(6)⁰ to 111.02(7)⁰ (Table 3). The Cr-O bond lengths in 1, range from 1.619(1) Å to 1.691 (1) Å. All structural parameters of 1 are in good agreement with those reported for other organic diammonium chromates like 1,4-butanediionium chromate²¹, 2,2-dimethyl-1,3-propanediionium chromate¹⁹. The Cr-O1 bond length of 1.691(1) Å is considerably longer than the other three Cr-O distances. We note that it is longer than the longest Cr-O distance of 1.667 Å reported for the 1,4-butanediionium chromate. The lengthening can
Table 1 — Technical details of data acquisition and selected refinement results for (enH2)[CrO4]1 and (enH2)[Cr2O7]2.

| Compound                  | Formula             | Temperature [K] | Wavelength [μm] | Space group | α [Å] | β [Å] | γ [Å] | Volume [Å³] | μ [mm⁻¹] | F(000) | Z | Molecular weight [g/mol] | Density (calc.) [g cm⁻³] | Φ | Crys tal size (in mm) | 20 range | Reflec tions collected | Reflec tions unique | Data (Fo>4σ(Fo)) | Rint | Min./Max. transmission | Δρ [e Å⁻³] | Parameters/Restrains | R1 for all Fo>4σ(Fo) | WR2 for all unique data | Goodness of fit | Ueq |
|---------------------------|---------------------|-----------------|-----------------|-------------|-------|-------|-------|-------------|----------|--------|---|------------------------|------------------------|---|----------------------|-----------|----------------------|----------------|----------------------|----------------|----------------|---------------------|---------|
| (enH2)[CrO4]1            | C2H2CrN2O4          | 293             | 71.073          | P2₁2₁2₁     | 6.656 | 8.869 | 11.833| 698.4(2)    | 368      | 178.12 | 4 | 1.59                  | 1.694                  | 4 | 0.16 × 0.1 × 0.05 | 3° - 60°  | 5213                  | 2041         | 1977                | 0.0342     | 0.5997 / 0.8406     | -0.59 / 0.32 | 85 / 0              | 0.0221     | 0.0590             | 1.104     |
| (enH2)[Cr2O7]2           | C2H2CrN2O7          |                 |                |             |       |       |       |             |          |        |   |                      |                        |   |                      |           |                      |               |                    |                |                  |                    |        |

be attributed to H bonding interactions. The O1 atom is involved in three short contacts to the H atoms of the organic dication (Table 4). In total, seven short contacts between the O atoms and the H atoms ranging from 1.897 to 2.597 Å are observed. O1 makes three short contacts while O3 is involved in two short contacts. The O2 and O4 atoms each have a single contact to a H of the cation. To the best of our knowledge, the O--H distance of 1.897 Å found in this complex is one of the shortest H-bonding distance observed in organic diammonium chromates. Interestingly, the shortest Cr-O bond of 1.619 Å is observed for Cr-O4 and the distance between O4 and H3 attached to N1 is the longest separation. In addition, the angle N1-H3--O4 of 111.12° indicates a

![Fig. 1 — Crystal structure of the cation and anion in (enH2)[CrO4]1 showing the atom–labelling scheme and displacement ellipsoids drawn at the 50% probability level.](image)

Table 2 — Atomic coordinates [x10⁴] and equivalent isotropic displacement parameters [Å²×10⁴] for (enH2)[CrO4]1 and (enH2)[Cr2O7]2

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Ueq is defined as one third of the trace of the orthogonalised Uij tensors.
very weak N–H interaction. Thus the lengthening of the Cr-O1 bond can be attributed to H-bonding interactions between the H atoms and the O atoms. The O–H network of (enH₂)[CrO₄] is presented in Fig. 2. As expected the O···H distances of the order of 2.0 Å are much shorter than the S···H distances observed in (enH₂)[WS₄] and other thiomolybdate containing organic cations.

**Crystal structure of (enH₂)[Cr₂O₇]²⁻**

The crystal structure of the dichromate complex 2 showing the atom-labelling scheme is displayed in Fig. 3. Selected bond lengths and bond angles for 2 are presented in Table 5. The structure consists of [Cr₂O₇]²⁻ anions, which are H-bonded to the organic dication. The O···Cr-O bond angles are very close to the tetrahedral values ranging from 107.45(8)° to 110.75(8)°. The Cr-O(terminal) bond distances range from 1.6075(15) to 1.6236(14) Å (Table 5). As expected the Cr-O2(bridging) bond length is significantly longer and amounts to 1.7767(9) Å. It is noted that a Cr-O(terminal) bond distance of 1.611(1) Å and Cr-O(bridging) distance of 1.78(1) Å has been reported for β-Na₂Cr₂O₇. The dichromate anions exhibit several H bonds to the organic dication. The Cr-O3 distance is considerably longer (1.6236 (14) Å) than the other Cr-O bond lengths. This lengthening can be again explained on the basis of different O···H bonding interactions. A total of five short contacts between the O atoms and the H atoms of (enH₂)⁺⁺⁺⁺ ranging from 1.946 to 2.500 Å are observed. O3 has

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**Table 4 — Hydrogen-bonding geometry (Å, °) for (enH₂)[CrO₄]¹⁻**

Fig. 2 — Crystal structure of 1 with view in the direction of the a-axis showing the hydrogen bonding network.
three short contacts while O1 and O4 are involved in only one contact each (Table 6). This feature explains the lengthening of the Cr-O3 bond as compared to the Cr-O4 and Cr-O1 bonds. The O···H distances in 2 are longer compared to the corresponding chromate salt. In Fig. 4 the resulting hydrogen bonded network is displayed. We note that the observed unit cell parameters and geometric parameters of 2 are in excellent agreement with those for the same complex isolated by a different synthetic route, i.e. a synthesis in a HF medium.

**Table 5 — Selected geometric parameters (\(\text{Å}^*\)) for**

\[
\begin{array}{ccc}
\text{Cr(1)-O(4)} & 1.6075 (15) & \text{Cr(1)-O(2)} & 1.7767 (9) \\
\text{Cr(1)-O(1)} & 1.6173 (15) & \text{N(1)-C(1)} & 1.487 (2) \\
\text{Cr(1)-O(3)} & 1.6236 (14) & \text{C(1)-C(1A)} & 1.508 (3) \\
\text{O(2)-Cr(1A)} & 1.7767 (9) & \\
\text{O(4)-Cr(1)-O(1)} & 109.40 (9) & \text{O(4)-Cr(1)-O(3)} & 110.99 (8) \\
\text{O(1)-Cr(1)-O(3)} & 110.75 (8) & \text{O(4)-Cr(1)-O(2)} & 109.68 (7) \\
\text{O(1)-Cr(1)-O(2)} & 108.52 (7) & \text{O(3)-Cr(1)-O(2)} & 107.45 (8) \\
\text{Cr(1A)-O(2)-Cr(1)} & 124.19 (11) & \text{N(1)-C(1)-C(1A)} & 110.43 (17) \\
\end{array}
\]

**Conclusions**

In the present study, the synthesis spectroscopic and X-ray structural characterization of two organic diammonium oxochromates are described. The simple cation exchange reaction described herein is a convenient method to prepare these complexes under ambient conditions. The O–H bonding interactions between the cation and anion seem to be the driving force for the formation of these organic oxochromates, because these interactions stabilize the overall structure. The short O···H contacts between the organic diammonium cation and the oxochromate dianion can also explain the lengthening of distinct Cr-O bond distances. Further experiments by using other organic ammonium halides are underway to test the generality of the cation exchange reaction and to

![Fig. 3 — Crystal structure of the cation and anion in (enH₂)[Cr₂O₇] showing the atom–labelling scheme and displacement ellipsoids drawn at the 50% probability level.](image)

![Fig. 4 — Crystal structure of 2 with view in the direction of the c-axis showing the hydrogen bonding network.](image)
understand the role of the alkyl groups in the lengthening of Cr-O bonds.

Supporting information available

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 196333 (1) and CCDC 196334 (2). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

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References