

Synthesis, characterization and structure of $[\text{Ni}(\text{H}_2\text{O})_6]_2(\text{Cr}_2\text{O}_7)_2(\text{hmta})_4 \cdot 2\text{H}_2\text{O}$ (hmta = hexamethylenetetramine): a novel metal organic–inorganic hybrid

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Abstract

A metal organic–inorganic hybrid compound $[\text{Ni}(\text{H}_2\text{O})_6]_2(\text{Cr}_2\text{O}_7)_2(\text{hmta})_4 \cdot 2\text{H}_2\text{O}$ was prepared and characterized by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.976(5) \text{ \AA}$, $b = 13.333(3) \text{ \AA}$, $c = 14.070(3) \text{ \AA}$, $\beta = 97.89^\circ(3)$, $Z = 4$ and $R = 0.048$. The structure consists of octahedrally coordinated nickel ions with water and discrete units of dichromate ions in which chromium is tetrahedrally coordinated. This inorganic moiety is well separated in the crystal structure from the organic moiety built by “hmta” ligands, resulting in the formation of a novel organic–inorganic framework.

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1. Introduction

$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is a compound known to mankind for a long time and the obvious question that

arises is whether or not the two ammonium cations could be substituted by a single divalent transition metal ion leading to a series of transition metal dichromates. Of the possible transition metal dichromates, only $\text{Ag}_2\text{Cr}_2\text{O}_7$ [1,2] and $\text{Cu-Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ [3] are known in the literature. Although, $\text{Fe}_2(\text{Cr}_2\text{O}_7)_3$ [4,5], and MnCr_2O_7 [6] are reported they are neither stable nor isolated and hence the composition and structure are

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unknown. However, they are stabilized on complexation with heterocyclic compounds such as pyridine, bipyridyl, and o-phenanthroline [7–11]. In an attempt to synthesize new transition metal dichromates, we found that one such heterocyclic neutral organic ligand, namely, hexamethylenetetramine (abbreviated as hmta hereafter) helps in stabilizing the metal dichromate salt.

Hmta is a unique molecule [11]. It has an adamantane type of structure consisting of three fused rings. The nitrogen atoms have lone pairs of electrons, which can be donated to a metal ion. In most complexes formed by hmta, tetradentate [12] or bidentate [13] character is exhibited. Here, we report the synthesis of a new hmta-stabilized divalent metal ion dichromate, $[\text{Ni}(\text{H}_2\text{O})_6](\text{Cr}_2\text{O}_7)(\text{hmta})_2 \cdot 2\text{H}_2\text{O}$.

2. Experimental procedure

The title compound was synthesized by mixing aqueous solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and hmta. Typically, 1 M solutions of the reactants were prepared and mixed in different proportions. A bright yellow precipitate was obtained when $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:(\text{NH}_4)_2\text{Cr}_2\text{O}_7:\text{hmta}$ ratio was 1:1:2. The precipitate was filtered, and air-dried at room temperature. Furthermore, any variation in the ratios in which the reactants were taken like 1:1:3 or 1:1:4 still leads to the formation of the compound with the same composition. The compound was recrystallized from water yielding yellow–orange crystals.

Quantitative estimation of nickel was done by gravimetric analysis while dichromate was estimated by volumetric analysis resulting in a ratio of 1:1 (nickel to dichromate).

Finally, to determine the structure and composition unambiguously, single-crystal X-ray diffraction studies were done with crystals of the compound.

Single crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer. The X-ray generator was operated at 50 kV and 40 mA using MoK_α radiation. Data were collected with a ω scan width of 0.3° . A total

of 606 frames per set were collected in three different settings of φ (0° , 90° and 180°) keeping the sample to detector distance of 6.03 cm and the 2θ value fixed at -25° . The data were reduced using the SAINTPLUS [14] and an empirical absorption correction was applied using SADABS [14]. The crystal structure was solved using direct methods by SIR92 [15] and refined by full matrix least squares using SHELXL [16]. The hydrogen atoms were located by difference Fourier technique and refined isotropically. Molecular and packing diagrams were generated by ORTEP32 [17] and CAMERON [18] present in the WINGX

Table 1
Crystal data of the compound

| Data | $[\text{Ni}(\text{H}_2\text{O})_6]_2(\text{Cr}_2\text{O}_7)_2(\text{hmta})_4 \cdot 2\text{H}_2\text{O}$ |
|--|---|
| Formula | $\text{C}_{12}\text{H}_{38}\text{Cr}_2\text{N}_8\text{Ni}_1\text{O}_{14}$ |
| Formula weight (/ g mol^{-1}) | 681.19 |
| Temperature/K | 293 (2) |
| Radiation | MoK_α |
| Wavelength (\AA) | 0.7107 |
| Crystal system | Monoclinic |
| Space group | $\text{P}2_1/\text{c}$ |
| $a/\text{\AA}$ | 27.976 (5) |
| $b/\text{\AA}$ | 13.333 (3) |
| $c/\text{\AA}$ | 14.070 (3) |
| $\alpha/^\circ$ | 90.000 |
| $\beta/^\circ$ | 97.896 (3) |
| $\gamma/^\circ$ | 90.000 |
| Volume (\AA^3) | 5198.41 (19) |
| Z | 8 |
| Density (g/cm^3) | 1.741 |
| Abs. Coeff. (mm^{-1}) | 1.62 |
| F(0 0 0) | 2832 |
| $\theta_{\text{min,max}}$ | 1.5, 25.5 |
| $h_{\text{min,max}}, k_{\text{min,max}}, l_{\text{min,max}}$ | −34, 34, −16, 16, −17, 17 |
| Number of reflections measured | 37222 |
| Number of unique reflections | 9189 |
| Number of parameters | 779 |
| Refinement method | Full matrix least squares on F^2 |
| R_{all} | 0.068 |
| R_{obs} | 0.048 |
| wR_2_{all} | 0.145 |
| wR_2_{obs} | 0.130 |
| $\Delta\rho_{\text{min,max}}$ ($\text{e}\text{\AA}^{-3}$) | −0.77, 1.09 |
| GooF | 1.34 |

(Version 1.64.03b) [19] program suite. The geometric calculations were done using PARST95 [20].

3. Results and discussion

Details of the crystal data are given in Table 1. Fig. 1a gives the ORTEP and Fig. 1b shows the packing diagram of the title compound. Table 2 lists the hydrogen bonding geometry.

The complex is made of two $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, two $\text{Cr}_2\text{O}_7^{2-}$, four hmta and two free water molecules in

the asymmetric unit. There are four such asymmetric units in the unit cell. The packing in the crystal structure generates an organic framework consisting of hmta and an inorganic framework consisting of dichromate anions (consisting of two dichromate anions, one of which is disordered) and octahedrally coordinated $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. The organic and the inorganic frameworks in this hybrid structure are held together by strong and highly directional O–H...N, O–H...O hydrogen bonds (Table 2). The organic moiety is held together by O–H...N hydrogen bonds, one with the oxygen from the water molecule, which in turn

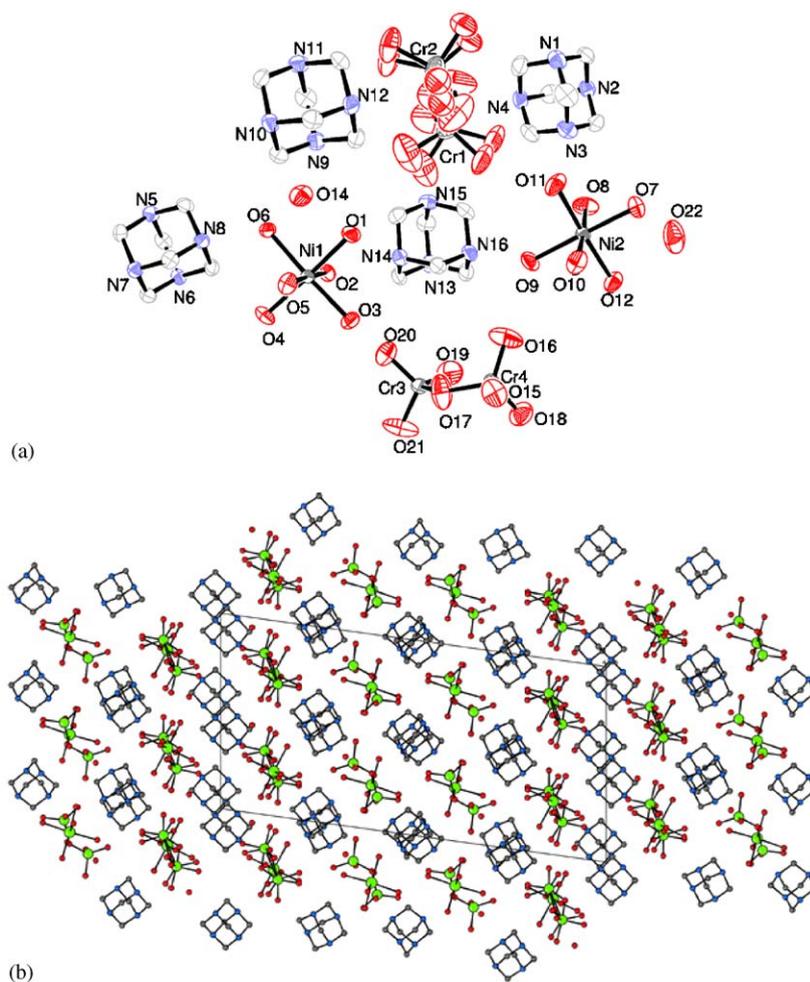


Fig. 1. (a) ORTEP diagram of the title compound (50% ellipsoidal probability). One of the dichromate ions is disordered (hydrogen atoms omitted for clarity); (b) packing diagram of the title compound.

Table 2
List of hydrogen bonding interactions

| | $d(\text{D-H})$ (Å) | $d(\text{H}\dots\text{A})$ (Å) | $d(\text{D}\dots\text{A})$ (Å) | $\angle \text{D-H}\dots\text{A}$ (°) |
|---------------|---------------------|--------------------------------|--------------------------------|--------------------------------------|
| O4-H53...N6 | 0.72 (5) | 2.16 (5) | 2.874 (4) | 177 (3) |
| O11-H64...N4 | 0.79 (5) | 2.01 (5) | 2.782 (6) | 166 (4) |
| O10-H73...N15 | 0.82 (5) | 2.34 (5) | 2.982 (5) | 135 (4) |
| O1-H58...N13 | 0.82 (5) | 2.06 (5) | 2.862 (5) | 168 (5) |
| O12-H61...N12 | 0.81 (5) | 1.95 (5) | 2.710 (5) | 156 (4) |
| O7-H63...N2 | 0.73 (5) | 2.06 (5) | 2.795 (4) | 176 (5) |
| O22-H70...N1 | 0.62 (6) | 2.22 (6) | 2.833 (6) | 172 (6) |

is coordinated to the nickel ion and the other with the oxygen atom of the free water molecule. The inorganic framework is held together by O–H...O hydrogen bonds. These bonds involve the oxygen of the dichromate ion and the oxygen atom of both the coordinated water molecule (with nickel) and the oxygen atom of the free water molecule. These hydrogen bonds, hence, use the water molecules to separate the organic and the inorganic moieties leading to water sandwiched hybrid. It is interesting to note that in this complex the conformation of the hmta moiety remains unaltered (Fig 1a).

4. Conclusion

Hexamethylenetetramine (hmta) has been employed as a fuel in the solution combustion synthesis which is a novel technique for the synthesis of simple and complex oxides and these new materials are known to exhibit interesting magnetic, electric and catalytic properties. The decomposition of these metal dichromate-hmt complexes is highly exothermic and the in situ heat generated could be utilized for the synthesis of complex oxides and these mostly belong to the family of perovskites and spinels. The same combustion process could be utilized for the preparation of high-surface area oxides such as ceria, zirconia and alumina which are used in catalysis, and in all these, hmt may act as a fuel. In addition to this, the compound could potentially be used for deposition of thin films using techniques such as dip-coating, etc. However,

much needs to be done to tap the potential of such compounds.

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Supplementary materials

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