

Synthesis and structure analysis of the bis(dicyclohexylammonium) chromate dihydrate complex, $[(C_6H_{11})_2NH_2]_2[CrO_4] \cdot 2H_2O$

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Abstract: A new bis(dicyclohexylammonium) chromate dihydrate complex, $[(C_6H_{11})_2NH_2]_2[CrO_4] \cdot 2H_2O$, (**I**), has been synthesized and its structure analyzed by FT-IR, EDS, elemental analysis, ICP-AES, and single crystal X-ray diffraction methods. The Cr(VI) complex (**I**) is tetragonal system, $\bar{I}42d$ space group with $a = 12.5196(1)$, $b = 12.5196(1)$, $c = 17.3796(3)\text{Å}$, $a = \beta = \gamma = 90^\circ$, $V = 2724.09(6)\text{Å}^3$, $Z = 4$. The crystal structure of complex (**I**) consists of tetrahedral chromate $[CrO_4]^{2-}$ anion, two organic dicyclohexylammonium $[(C_6H_{11})_2NH_2]^+$ cations and two lattice water molecules. The chromate anion and protonated dicyclohexylammonium cation is mainly constructed through the ionic bond. The cyclohexylammonium rings of the dicyclohexylammonium cation take the chair form and vertical configuration with each other. The N-H \cdots O and O-H \cdots O hydrogen bond networks between the N_{dicyclohexylammonium}, O_{water} and O_{chromate} atom lead to self-assembled molecular conformation and stabilize the crystal structure.

Key words: chromate complex, dicyclohexylammonium ligand, crystal structure, hydrogen bonding

1. Introduction

Most heavy metal ions such as chromium, lead, cadmium, mercury, copper and zinc are well-known as toxic, carcinogenic and mutagenic agents, and giving a serious effect to human populations and various organisms.^{1,2} However, the wastes and waste waters from many industries such as the leather tanning, textile and electroplating are chromium-rich in hexavalent and trivalent forms. Especially, the hexavalent chromium form is more hazardous than the trivalent form and tends to form poly oxoanions as unstable intermediates.^{3,4} Therefore, the discharge of these metal ions into aquatic bodies and sources of

drinking water must be strictly controlled.

There are many investigations for heavy metal remediation, including chemical precipitation, activated carbon adsorption, electrolytic treatment, *in situ* vitrification and biological treatment.⁵⁻⁷ To remove the heavy metal ions from waters and industrial residues, the chemical precipitation is one of the most efficient and cheap methods. However, chemical precipitation process for chromium remediation may require reduction of the Cr(VI) to Cr(III) and may not be effective in waste water remediation.⁸ In addition, this process requires some chemicals for pH control and reduction. On the other hand, organic ligand process has a good capacity to removing

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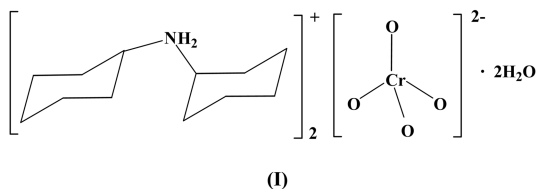


Fig. 1. Chemical structural diagram of complex (I).

heavy metals in wastewater compared with traditional chemical treatment or precipitation process.^{9,10} Organic ligands can easily control the reaction selectivity between heavy metal ions by various functional groups and increase the stability of chelate complex formed by metal ions.

In our group, research has been focused on the development of new heavy metal remediation agents containing hard amine donor, carboxylate donor and soft thiolate donor.¹¹⁻¹⁴ Herein, we report the synthesis and structure analysis of the chromium (VI) complex (I), with dicyclohexylammonium ligand as known as hard amine donor (Fig. 1).

2. Experimental

2.1. Synthesis and analysis of complex (I)

Dicyclohexylamine (*ca.* 5 mL, 20 mmol) was added in an aqueous solution (10 mL) of $K_2Cr_2O_7$ (2.94 g, 10 mmol). The mixture solution was adjusted to pH 9 by adding 2-aminoethanol. After a small amount of the precipitate was filtered off, the aqueous solution was allowed to stand in a refrigerator at 278 K. After three weeks, yellow crystals of suitable for single crystal X-ray diffraction were obtained.

The FT-IR spectrum in the 400~4000 cm^{-1} region for the complex (I) was obtained by the KBr pellet method on a BioRad Digilab FTS-165 infrared spectrophotometer at ambient temperature. The EDS spectrum obtained on an EDAX Phoenix energy dispersive X-ray spectrometer with Philips XL-30S FEG scanning electron microscope. The contents of the carbon, hydrogen, nitrogen and chromium were analyzed by CE EA-1110 elemental analyzer and Jobin-Yvon Ultima-C inductively coupled plasma-

atomic emission spectrometer, respectively. Analysis calculated for $C_{24}H_{52}N_2O_6Cr$: C 55.79, H 10.14, N 5.42, O 18.58, Cr 10.06%; found: C 55.69, H 10.17, N 5.37, Cr 10.00%.

2.2. X-ray crystallography

A yellow block crystal (dimensions 0.38 × 0.30 × 0.24 mm) was selected for single crystal X-ray analysis. The crystal was coated with epoxy glue in order to prevent spontaneous liberation of dicyclohexylamine ligand and water molecules from the specimen under ambient conditions. The epoxy-coated crystal was mounted on a Bruker SMART APEX II X-ray diffractometer equipped with a graphite-monochromated $Mo\ K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) and a CCD area detector. The intensity data were collected in the phi and omega scan mode with operating 50 kV, 30 mA at 293 K.¹⁵ The data reduction was performed using the SAINT and SADABS programs.¹⁶

All calculations in the structural solution and refinement were performed using the Bruker SHELXTL program.¹⁷ The structure was solved by the heavy atom method and refined by full-matrix least-squares methods. All the non-hydrogen atoms were refined with anisotropically; the hydrogen atoms were geometrically positioned and fixed with the isotropic thermal parameters. Final difference of electron density maps contained no significant features.

3. Results and Discussion

The structural features of complex (I) was identified to the basis FT-IR, EDS, elemental analysis and ICP-AES analysis. The dicyclohexylamine ligand and water molecules were assigned by the relevant FT-IR absorption bands, respectively.¹⁸ The EDS spectrum showed the presence of C, N, O and Cr. The composition of the crystal was deduced from the elemental analysis and ICP-AES analysis; the formula of $[(C_6H_{11})_2NH_2]_2[CrO_4] \cdot 2H_2O$, (I), is consistent with the results of single-crystal X-ray diffraction analysis.

The crystallographic data and structure refinement parameters of the complex (I) are summarized in

Table 1. Crystallographic data for complex (I)

Formula	C ₂₄ H ₅₂ N ₂ O ₆ Cr
Formula weight	516.68
Crystal system	tetragonal
Space group	$\bar{4}2d$
<i>a</i> (Å)	12.5196(1)
<i>b</i> (Å)	12.5196(1)
<i>c</i> (Å)	17.3796(3)
<i>a</i> = <i>β</i> = <i>γ</i> (°)	90
<i>V</i> (Å ³)	2724.09(6)
<i>Z</i>	4
<i>D_c</i> (g/cm ³)	1.260
<i>μ</i> (Mo-Kα) (mm ⁻¹)	0.459
<i>F</i> (000)	1128
θ range for data collection (°)	4.0–56.5
Index range	-11 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 10, -23 ≤ <i>l</i> ≤ 15
Reflections collected	6707
Independent reflections	1636 [<i>R</i> _{int} = 0.0202]
Data/restraints/parameters	1636/0/80
Goodness-of-fit on <i>F</i> ²	1.105
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0229, <i>wR</i> ₂ = 0.0684

Table 1. The selected bond lengths and bond angles are listed in Table 2. The chemical structural diagram and a typical ORTEP view of complex (I) are shown in Figs. 1 and 2, respectively. The molecular structure of Cr(VI) complex (I) consists of negatively charged chromate anion, protonated dicyclohexylammonium cation and water molecules in a 1:2:2 ratio. The central Cr(VI) ions has a tetrahedron geometry with

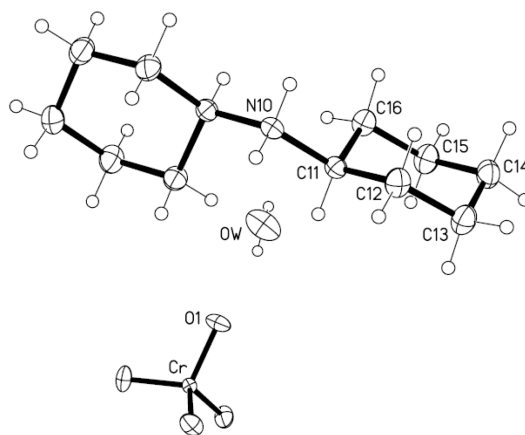


Fig. 2. ORTEP view of the complex (I) with the atomic numbering scheme and 30% probability displacement ellipsoids.

four oxygen atoms. Bond lengths and angles around the Cr(VI) atom are 1.643(1) Å and 108.96(4)°, 110.50(8)°, respectively. The cyclohexylammonium rings of the protonated dicyclohexylammonium cation take the chair form and vertical configuration with each other. As listed in Table 2, the bond lengths and angles of dicyclohexylammonium are in normal ranges and are comparable to those of the previously reported similar structure [C₆H₁₁NH₃]₂[CrO₄].¹³ The chromate anion and protonated dicyclohexylammonium cation is mainly constructed through the ionic bond.

As shown in Fig. 3, the crystal-packing diagram of

Table 2. Selected bond lengths (Å) and angles (°) for complex (I)

Cr-O(1)	1.643(1)	Cr-O(1) ⁱ	1.643(1)
Cr-O(1) ⁱⁱ	1.643(1)	Cr-O(1) ⁱⁱⁱ	1.643(1)
N(10)-C(11)	1.504(1)	N(10)-C(11) ^{iv}	1.504(1)
C(11)-C(12)	1.523(2)	C(12)-C(13)	1.527(2)
C(13)-C(14)	1.510(2)	C(14)-C(15)	1.515(2)
C(15)-C(16)	1.526(2)	C(16)-C(11)	1.519(2)
O(1)-Cr-O(1) ⁱ	108.96(4)	O(1)-Cr-O(1) ⁱⁱ	108.96(4)
O(1) ⁱ -Cr-O(1) ⁱⁱ	110.50(8)	O(1) ⁱ -Cr-O(1) ⁱⁱⁱ	110.50(8)
O(1) ⁱ -Cr-O(1) ⁱⁱⁱ	108.96(4)	O(1) ⁱⁱ -Cr-O(1) ⁱⁱⁱ	108.96(4)
N(10)-C(11)-C(12)	107.6(1)	N(10)-C(11)-C(16)	111.2(1)
C(11)-C(12)-C(13)	110.6(1)	C(12)-C(13)-C(14)	111.7(1)
C(13)-C(14)-C(15)	111.3(1)	C(14)-C(15)-C(16)	111.5(1)
C(15)-C(16)-C(11)	110.5(1)	C(16)-C(11)-C(12)	111.3(1)
C(11)-N(10)-C(11) ^{iv}	118.0(1)		

Symmetry transformations used to generate equivalent atoms: ⁱ -*y*, *x*, -*z*, ⁱⁱ *y*, -*x*, -*z*, ⁱⁱⁱ -*x*, -*y*, *z*, ^{iv} *x*+0, -*y*+1/2, -*z*+1/4.

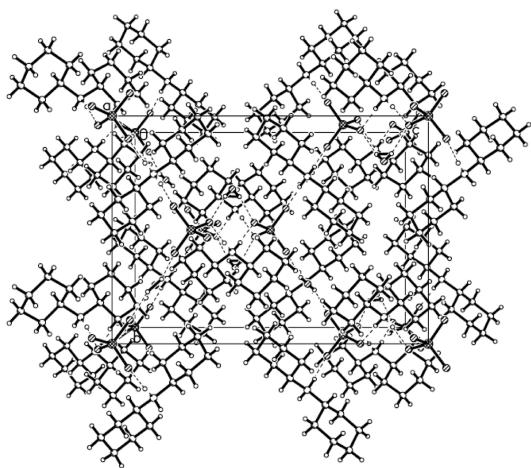


Fig. 3. Perspective view of the complex (I) along the *a* axis; hydrogen bonds are shown by broken lines.

this complex reveals a discreted structure. There are inter-molecular hydrogen bonds between the N-H moieties of the [(C₆H₁₁)₂NH₂]⁺ cation, the O atoms of the water molecules and the O atoms of the [CrO₄]²⁻ anion: N(10)-H(10a)⋯O(1) 2.791(1)Å, 175.9°; N(10)-H(10b)⋯O(1) 2.791(1)Å, 175.9°; O(W)-H(Wa)⋯O(1) 2.932(2)Å, 165.5(5)°. The N-H⋯O and O-H⋯O hydrogen bonds are linked together in zig-zag chains. These hydrogen bond interactions lead to self-assembled molecular conformation and contribute to stabilization of the crystal structure.

4. Supplementary Material

Complete lists of atomic coordinates, anisotropic displacement parameters, torsional angles, hydrogen atom coordinates, and structure factors for title complex are available.

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