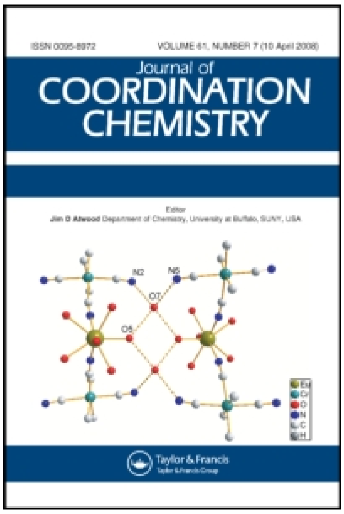

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PREPARATION AND CRYSTAL STRUCTURE OF DICYCLOHEXYLAMMONIUM CHROMATE $[C_6H_{11}NH_3]_2[C_rO_4]$

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A novel two-dimensional Cr(VI) complex, $[C_6H_{11}NH_3]_2[CrO_4]$, has been prepared and structurally characterized by X-ray diffraction methods. The complex is triclinic, space group $P\bar{1}$ with $a = 6.575(2)$, $b = 8.384(2)$, $c = 15.075(3)$ Å, $\alpha = 75.14(2)$, $\beta = 78.09(2)$, $\gamma = 89.45(2)°$, $V = 785.1(3)$ Å^3, $Z = 2$. The crystal structure of the complex consists of tetrahedral $[CrO_4]^{2-}$ dianion layers and organic $[C_6H_{11}NH_3]^+$ cation layers. The chromate anions and protonated cyclohexylammonium cations are mainly stabilized through ionic bonding. An N–H···O hydrogen bond network between the $N_{cyclohexylammonium}$ and $O_{chromate}$ atoms ensures the cohesion and stability of the crystal structure.

Keywords: Chromate complex; Cyclohexylamine; Crystal structure; Hydrogen bond

INTRODUCTION

Most heavy metals such as chromium, copper, cadmium, lead, mercury and zinc are well known as toxic, carcinogenic and mutagenic agents, and give rise to serious health effects [1–3]. However, many industries use heavy metals in manufacturing such as of products textiles, leather tanning and electroplating. The wastes and wastewaters from these industries are chromium-rich in hexavalent and/or trivalent forms. The hexavalent chromium form is more hazardous than the trivalent form [4]. Therefore, the discharge of these metals into aquatic bodies and sources of drinking water must be strictly controlled.

There are many investigations concerning remediation of heavy-metal contamination, including chemical precipitation, activated carbon adsorption, electrolytic treatment, *in-situ* vitrification and biological treatments [5–7]. Chemical precipitation is one of the most efficient and cheap methods to remove heavy metal ions from waters and industrial residues. For example, chemical treatments using sulfides and hydroxides have been investigated. However, a considerable concentration of toxic heavy metals

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remain in wastewater after chemical treatment or precipitation processes. These traditional processes are not efficient enough to satisfy pollution control limits [8]. Indeed, chemical precipitation of chromium may require reduction of Cr(VI) to Cr(III) and may not be effective in wastewater remediation [9]. In addition, precipitation has some disadvantages such as the need for additional chemicals for pH control and reduction.

Organic ligand processes have a good capacity for removing heavy metals in wastewater compared with traditional chemical treatment or precipitation [10–13]. Organic ligands can control reaction selectivity between heavy metal ions by involvement of various functional groups and can increase the stability of complex or chelate compounds formed by the metal ions.

Our research has focused on the development of new heavy metal remediation agents containing amine, carboxylate donor and/or thiolate donors [14,15]. In this paper, we report the preparation and crystal structure of dicyclohexylammonium chromate(VI).

EXPERIMENTAL

Synthesis and Analysis of $[C_6H_{11}NH_3]_2[CrO_4]$

Cyclohexylamine (ca 5 cm^3, 40 mmol) was added to an aqueous solution (10 cm^3) of $K_2Cr_2O_7$ (2.94 g, 10 mmol). The pH of the mixture was adjusted to 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 a few days, yellow crystals were obtained.

The IR spectrum of the crystal was recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using KBr wafers. Cyclohexylamine was assigned by the relevant IR absorption bands [16]. EDS spectra obtained on a Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy-dispersive X-ray spectrometer showed the presence of C, N, O and Cr. Carbon, hydrogen, nitrogen and oxygen contents were determined by a CE EA-1110 elemental analyzer. Cr was determined by a Jobin-Yvon Ultima-C inductively coupled plasma emission spectrometer. The composition of the crystals was deduced from elemental analyses; the formula of $[C_6H_{11}NH_3]_2[CrO_4]$ is consistent with the results of single crystal X-ray diffraction analysis. Yield: *ca* 50%. *Anal.* Calcd. for $C_{12}H_{28}N_2O_4Cr$ (%): C, 45.56; H, 8.92; N, 8.86; O, 20.23; Cr, 16.44. Found: C, 45.36; H, 8.94; N, 8.90; Cr, 16.30.

X-Ray Crystallography

A yellow blocky crystal of the title compound was coated with epoxy glue in order to prevent spontaneous liberation of cyclohexylamine from the specimen under ambient conditions. The epoxy-coated crystal was mounted on a Bruker P4 four-circle X-ray diffractometer and intensity data were collected in the θ–2θ scan mode using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters and an orientation matrix for the compound were determined from a least-squares fit of 44 accurately centred reflections with a θ range of 4.87 to 12.53°. Three standard reflections were monitored every 97 reflections; no noticeable decay was observed through

TABLE I Crystal data and structure refinement details for $[C_6H_{11}NH_3]_2[CrO_4]$

Chemical formula	$C_{12}H_{28}N_2O_4Cr$
Formula weight	316.36
Temperature (*K*)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a (Å) = 6.575(2) b (Å) = 8.384(2) c (Å) = 15.075(3) α (°) = 75.14(2) β (°) = 78.09(2) γ (°) = 89.45(2)
V (Å^3)	785.1(3)
Z	2
Density (calculated) (g cm^{-3})	1.338
μ(Mo Kα) (mm^{-1})	0.740
F(000)	340
θ range for data collection (°)	2.52 ~ 26.49
Index range	$-1 \leq h \leq 8$, $-10 \leq k \leq 10$, $-17 \leq l \leq 18$
Reflections measured	3105
Independent reflections	2546 ($R_{\text{int}} = 0.0202$)
Data/restraints/parameters	2546/0/175
Goodness of fit on F^2	1.083
Final R indices [$I > 2\sigma(I)$]	0.0664, 0.1704
R indices (all data)	0.0718, 0.1776

the data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on psi-scans was applied [17].

All calculations in the structure solution and refinement were performed using the Bruker SHELXTL crystallographic software package [18]. The space group assigned based on systematic absences and intensity statistics, as confirmed by the successful refinement. The structure was solved by the direct method [19] and refined by successive full-matrix least-squares methods followed by difference Fourier maps. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions with isotropic thermal parameters. Final electron density maps contained no significant features. Further crystallographic and experimental data are given in Table I.

RESULTS AND DISCUSSION

Refined atomic parameters and selected bond lengths and angles for $[C_6H_{11}NH_3]_2$ $[CrO_4]$ are listed in Tables II and III, respectively. The molecular structure with atom numbering and a crystal packing diagram are shown in Figs. 1 and 2, respectively.

As shown in Fig. 1, the molecular structure consists of negatively charged chromate anions and protonated cyclohexylammonium cations in a 1:2 ratio. The coordination environment around the central Cr(VI) ions is a slightly distorted tetrahedron with four oxygen atoms. Bond lengths and angles around the Cr(VI) atom lie in the range 1.614(2) to 1.676(2) Å and 108.1(1) to 111.0(1)°, respectively. Two cyclohexylammonium cations take the chair conformation. As listed in Table III, bond lengths and angles in the cation are not unusual.

TABLE II Atomic coordinates and equivalent thermal parameters for $[C_6H_{11}NH_3]_2[CrO_4]$

	x/a	y/b	z/c	U_{eq} ($Å^2$)
Cr	0.7283(1)	0.7013(1)	0.5187(1)	0.031(1)
O(1)	0.8390(4)	0.7363(3)	0.4067(2)	0.042(1)
O(2)	0.8822(4)	0.7888(3)	0.5706(2)	0.041(1)
O(3)	0.4988(4)	0.7832(3)	0.5326(2)	0.042(1)
O(4)	0.7047(4)	0.5049(3)	0.5662(2)	0.050(1)
N(10)	0.7568(4)	1.0933(3)	0.5954(2)	0.039(1)
C(11)	0.6534(5)	1.0709(4)	0.6956(2)	0.031(1)
C(12)	0.8028(6)	0.9956(5)	0.7584(3)	0.042(1)
C(13)	0.6988(7)	0.9664(6)	0.8613(3)	0.059(1)
C(14)	0.5003(7)	0.8613(5)	0.8855(3)	0.055(1)
C(15)	0.3511(6)	0.9317(5)	0.8226(3)	0.047(1)
C(16)	0.4546(5)	0.9644(4)	0.7187(3)	0.041(1)
N(20)	1.1653(4)	0.5701(3)	0.6324(2)	0.036(1)
C(21)	1.1263(5)	0.5432(4)	0.7352(2)	0.032(1)
C(22)	1.2841(6)	0.4282(5)	0.7758(3)	0.045(1)
C(23)	1.2378(6)	0.3918(6)	0.8826(3)	0.054(1)
C(24)	1.0167(7)	0.3253(5)	0.9255(3)	0.054(1)
C(25)	0.8610(6)	0.4409(6)	0.8843(3)	0.053(1)
C(26)	0.9040(5)	0.4749(5)	0.7782(3)	0.040(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and angles (°) for $[C_6H_{11}NH_3]_2[CrO_4]$

Cr–O(1)	1.646(2)	Cr–O(2)	1.676(2)
Cr–O(3)	1.648(2)	Cr–O(4)	1.614(2)
N(10)–C(11)	1.488(4)	C(11)–C(12)	1.524(4)
C(12)–C(13)	1.519(6)	C(13)–C(14)	1.508(6)
C(14)–C(15)	1.515(6)	C(15)–C(16)	1.527(5)
C(16)–C(11)	1.517(5)	N(20)–C(21)	1.475(4)
C(21)–C(22)	1.524(4)	C(22)–C(23)	1.526(5)
C(23)–C(24)	1.512(6)	C(24)–C(25)	1.519(6)
C(25)–C(26)	1.517(5)	C(26)–C(21)	1.523(5)
O(1)–Cr–O(2)	108.1(1)	O(1)–Cr–O(3)	111.0(1)
O(1)–Cr–O(4)	109.6(1)	O(2)–Cr–O(3)	108.7(1)
O(2)–Cr–O(4)	109.3(1)	O(3)–Cr–O(4)	110.2(1)
N(10)–C(11)–C(12)	109.7(3)	N(10)–C(11)–C(16)	110.0(3)
C(11)–C(12)–C(13)	110.8(3)	C(12)–C(13)–C(14)	111.5(3)
C(13)–C(14)–C(15)	112.3(3)	C(14)–C(15)–C(16)	111.8(3)
C(15)–C(16)–C(11)	111.1(3)	C(16)–C(11)–C(12)	111.5(3)
N(20)–C(21)–C(22)	110.3(3)	N(20)–C(21)–C(26)	109.4(3)
C(21)–C(22)–C(23)	110.8(3)	C(22)–C(23)–C(24)	111.7(3)
C(23)–C(24)–C(25)	111.4(4)	C(24)–C(25)–C(26)	111.3(3)
C(25)–C(26)–C(21)	110.7(3)	C(26)–C(21)–C(22)	111.7(3)

The crystal packing diagram of this complex reveals a layered, two-dimensional structure composed of chromate anion and cyclohexylammonium cation layers as shown in Fig. 2. The layers are linked together in chains along the *a* direction by an N–H···O hydrogen bond, and the chains are inter-linked in the *ab* plane by hydrogen bonds. There exist many intra- and inter-molecular hydrogen bonds between the O atoms of the $[CrO_4]^{2-}$ anion and the N–H moieties of the $[C_6H_{11}NH_3]^+$ cation: N(10)–H(10a)···O(1) 3.020(4) Å, 162.6°; N(10)–H(10a)···O(2) 3.032(4) Å, 122.8°; N(10)–H(10b)···O(3) 2.811(4) Å, 169.3°; N(10)–H(10c)···O(2) 2.767(4) Å,

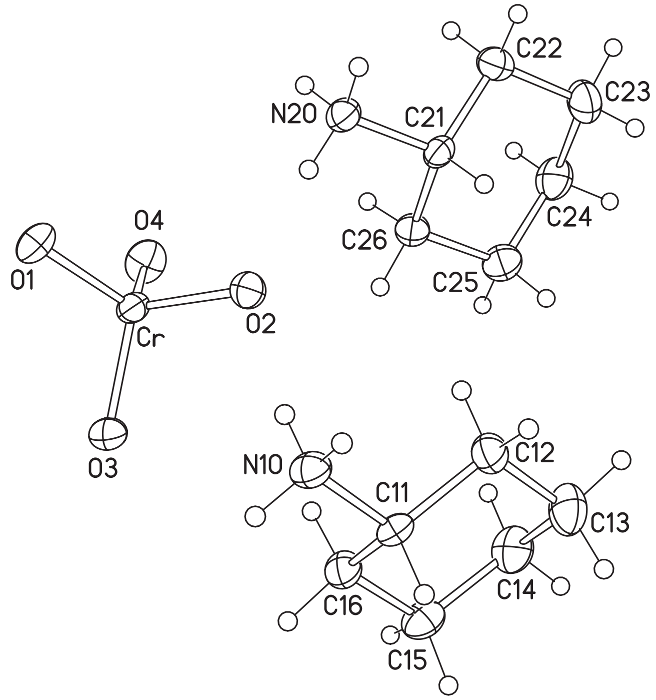

FIGURE 1 ORTEP drawing of $[C_6H_{11}NH_3]_2[CrO_4]$ with the atom numbering. Thermal ellipsoids are drawn at 30 % probability level.

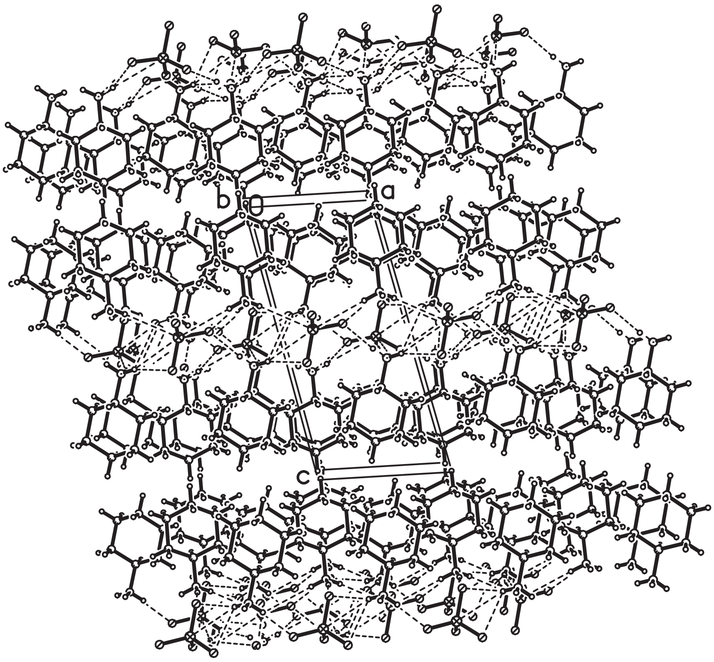

FIGURE 2 Crystal packing diagram of $[C_6H_{11}NH_3]_2[CrO_4]$ viewed along the *b* axis.

172.4°; N(20)–H(20a)···O(2) 2.733(3) Å, 174.4°; N(20)–H(20b)···O(1) 2.781(3) Å, 173.3°; N(20)–H(20c)···O(3) 2.757(4) Å, 156.5°. This combination of strong and weak hydrogen bonds between anions and cations contributes to the stabilization of the crystal structure.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request and have been deposited as CCDC-221103 in the Cambridge Crystallographic Database.

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