

## Crystal Structure and Hirshfeld Surface Analysis of Potassium *sym-fac-Bis*(*N*-methyliminodiacetato)chromate(III)

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The structure of  $K[Cr(C_5H_7NO_4)_2]$  ( $C_5H_7NO_4$  is methyliminodiacetate; mida) was confirmed from synchrotron X-ray data at 173 K. The complex crystallized in the space group  $C2/c$  of the monoclinic system with four mononuclear formula units in a cell of dimensions  $a = 16.875(3)$ ,  $b = 6.3970(3)$ ,  $c = 13.784(3)$  Å and  $\beta = 113.81(3)^\circ$ . The Cr(III) ion is located on a center of symmetry with one independent Cr–N bond length of 2.0740 (14) Å and two Cr–O bond lengths of 1.9547 (12) and 1.9661 (12) Å. The Cr(III) ion is coordinated by two N atoms and four O atoms of symmetrical-facial mida ligands, displaying a distorted octahedral geometry. Hirshfeld surface analysis with 2D fingerprint plots revealed that the O...H, H...H and O...K interactions are the main intermolecular interactions. The crystal structure is stabilized by the O...H, H...H and O...K interactions among potassium cation, H atoms and O atoms of carboxylate group from neighbouring mida groups.

**Keywords:** Crystal structure, Synchrotron radiation, Potassium salt, *Sym-facial* configuration, Hirshfeld-surface analysis.

### INTRODUCTION

An octahedral chromium(III) complexes with two tridentate iminodiacetate (ida) or *N*-methyliminodiacetate (mida;  $C_5H_7NO_4$ ) ligands can coordinate to a central metal ion as a tridentate ligand through one N atom and two O atoms. The *bis*(tridentate)chromate(III) complex with *N*-alkyliminodiacetate ion can form three configurational isomers potentially (Fig. 1).

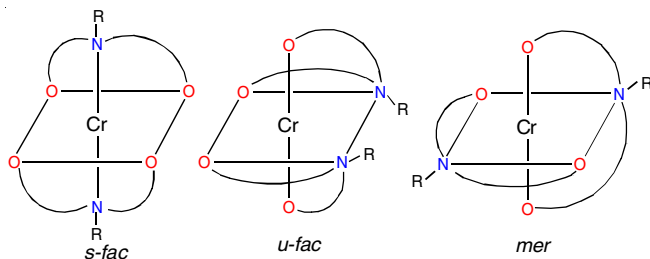
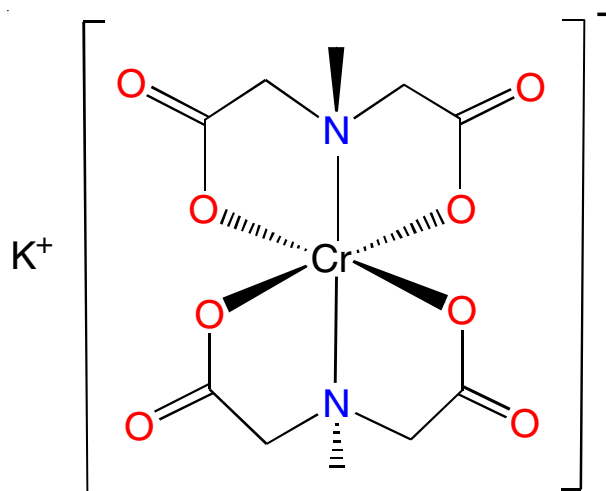


Fig. 1. Three possible geometrical isomers of  $[Cr(R-ida)_2]$

The ligand mida differs from iminodiacetate (ida) in the substitution of imino hydrogen with methyl group. This change in the structure has significant consequences in the geometry of *bis*chromate(III) complexes with these ligands. Two facial

configurations in *cis* (unsymmetrical-facial, *u-fac*) or *trans* (symmetrical-facial, *s-fac*) geometry with respect to the two N atoms have been observed: for example  $K[Cr(ida)_2] \cdot 3H_2O$  [1] and  $Na[Cr(ida)_2] \cdot 1.5H_2O$  [2] are *u-fac* structures while  $Na[Cr(mida)_2]$  and  $[(NH_4)_{0.8}K_{0.2}][Cr(mida)_2]$  are *s-fac* structures [3,4]. The substituent  $R = i-C_3H_7$  or *tert*- $C_4H_9$  also yielded *s-fac* configuration [5,6]. The structural analysis of  $(NH_4)[Cr(pydc)_2]$  shows that the two tridentate pyridine-2,6-dicarboxylate (pydc) dianions octahedrally coordinate to the Cr metal center through one N atom and two carboxylate O atoms in a *trans* meridional arrangement [7]. The *trans* meridional isomer was also found in the structure of  $Na[Fe(mida)_2](NaClO_4)_2 \cdot 3H_2O$  [8]. A search of the Cambridge Structural Database (Version 5.38, May 2017 with 3 updates) [9] gave just two hits for a complex anion  $[Cr(C_5H_7NO_4)_2]^-$  unit. The crystal structures of  $Na[Cr(mida)_2]$  with three different space groups have been reported and compared previously [3,10]. Recently, we have reported the crystal structure of  $[(NH_4)_{0.8}K_{0.2}][Cr(mida)_2]$  [4]. However, no structure of  $[Cr(mida)_2]^-$  with pure potassium cation has been deposited. Here we report the crystal structure of  $K[Cr(C_5H_7NO_4)_2]$ , (**Scheme-I**) in order to clarify unambiguously the bonding mode of the two methyliminodiacetato ligands and the geometrical arrangement of neat potassium salt.

Scheme-I: Chemical structure of  $K[Cr(mida)_2]$ 

## EXPERIMENTAL

All the chemicals were of reagent-grade materials and used without further purification. The starting material,  $K[Cr(mida)_2]$  was prepared by a method similar to that outlined previously [11]. The crude potassium salt (0.20 g) was dissolved in 15 mL of water at 323 K. The resulting solution was filtered to remove any impurities and allowed to stand at room temperature for several days to give pale orange block-like crystals of potassium salt suitable for X-ray diffraction analysis.

**Crystal structure analysis:** A block-shaped pale orange crystal of title complex with approximate dimensions 0.08 mm  $\times$  0.08 mm  $\times$  0.07 mm was coated with paratone-*N* oil to prevent crystallinity losses on exposure to air. The diffraction data were measured with synchrotron radiation on a BL2D SMC ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator (0.610 Å) at the Pohang Accelerator Laboratory, Korea and with a nitrogen cold stream (173 K). The PAL BL2D-SMDC Program [12] was used for collection of data, and HKL3000sm (v715) [13] was used for cell refinement, reduction, and absorption correction. The crystal structure was solved by the direct method with SHELXT-2014 program and refined by full-matrix least-squares calculations with the SHELXL-2017 program package [14]. Molecular graphics were produced using DIAMOND-3 [15]. Non-hydrogen atoms were refined anisotropically. C-bound H atoms in the complex were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.98–0.99 Å with  $U_{iso}(H)$  values of 1.5 and 1.2  $U_{eq}$  of the parent atoms respectively. The crystallographic experimental data and refinement parameters are summarized in Table-1

## RESULTS AND DISCUSSION

**Crystallography:** The single-crystal X-ray structure analysis indicated that the title complex consisted of a  $[Cr(C_5H_7NO_4)_2]^-$  anion and one potassium cation, with monoclinic space group of C2/c with  $Z = 4$ . Selected bond lengths and angles are given in Table-2. An ellipsoid plot of the complex molecule together with atomic numbering is illustrated in Fig. 2. Hydrogen atoms are shown as circles of arbitrary radii.

TABLE-1  
CRYSTALLOGRAPHIC DATA FOR THE TITLE COMPLEX

Chemical formula	$K[Cr(C_5H_7NO_4)_2]$
$M_r$ (g mol <sup>-1</sup> )	381.33
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	173 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.875(3), 6.3970(3), 13.784(3)
$\beta$ (°)	113.81(3)
<i>V</i> (Å <sup>3</sup> )	1361.4(6)
<i>Z</i>	4
Radiation type, $\lambda$ (Å)	Synchrotron, 0.610
$\mu$ (mm <sup>-1</sup> )	0.78
Crystal size (mm <sup>3</sup> )	0.08 $\times$ 0.08 $\times$ 0.07
Data collection	ADSC Q210 CCD area detector diffractometer
$T_{min}$ , $T_{max}$	0.804, 1.000
No. of independent reflections	6665
$R_{int}$	0.055
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>	0.034, 0.0946, 1.04
No. of measured reflections	1981
No. of parameters	104
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.61, -0.78

TABLE-2  
SELECTED BOND DISTANCES (Å) AND  
ANGLES (°) FOR THE TITLE COMPLEX

Cr1–O3	1.9547 (12)	O2–C1	1.227 (2)
Cr1–O1	1.9661 (12)	O3–C3	1.2905 (19)
Cr1–N1	2.0740 (13)	O4–C3	1.228 (2)
K1–O4	2.7745 (13)	N1–C2	1.4851 (19)
K1–O2 <sup>i</sup>	2.8584 (16)	N1–C5	1.486 (2)
K1–O1 <sup>i</sup>	2.8851 (13)	N1–C4	1.497 (2)
K1–O3	2.9341 (13)	C1–C2	1.521 (2)
O1–C1	1.2912 (19)	C3–C4	1.512 (2)
O3–Cr1–O3 <sup>ii</sup>	180.00 (7)	C5–N1–C4	110.30 (14)
O3–Cr1–O1	90.57 (5)	C2–N1–Cr1	105.57 (9)
O3 <sup>ii</sup> –Cr1–O1	89.43 (5)	C5–N1–Cr1	113.49 (10)
O3–Cr1–N1	85.13 (6)	C4–N1–Cr1	106.76 (10)
O1 <sup>ii</sup> –Cr1–N1	97.14 (5)	O2–C1–O1	123.92 (16)
O1–Cr1–N1	82.86 (5)	O2–C1–C2	120.12 (14)
N1 <sup>ii</sup> –Cr1–N1	180.0	O1–C1–C2	115.92 (13)
O4–K1–O3	45.69 (4)	N1–C2–C1	112.06 (12)
C1–O1–Cr1	116.26 (10)	O4–C3–O3	123.79 (15)
C3–O3–Cr1	116.47 (10)	O4–C3–C4	118.82 (15)
C3–O3–K1	90.69 (9)	O3–C3–C4	117.40 (14)
Cr1–O3–K1	152.73 (5)	O4–C3–K1	58.12 (9)
C3–O4–K1	99.82 (10)	O3–C3–K1	65.68 (8)
C2–N1–C5	109.93 (13)	C4–C3–K1	176.74 (11)
C2–N1–C4	110.67 (14)	N1–C4–C3	114.11 (14)

Symmetry codes: (i)  $x, -y, z-1/2$ ; (ii)  $-x+1, -y+1, -z+1$ .

Counter ionic species play an important role in crystal packing and hydrogen bonding pattern. The structure reported here is another example of a  $[Cr(mida)_2]^-$  salt but with a different cation [3,4,10]. The structural analysis shows that the two tridentate methyliminodiacetate dianions octahedrally coordinate to the Cr metal center through one N atom and two carboxylate O atoms in a symmetrical-facial configuration. The coordinated N atoms are mutually *trans* (*s-fac*) arrangement. The facial configuration of (I) can be compared with the *cis(u-fac)* geometry of  $K[Cr(ida)_2] \cdot 3H_2O$  [1],  $Ca[Cr(ida)_2] \cdot 9H_2O$  [16] and  $Na[Cr(ida)_2] \cdot 1.5H_2O$  [2]. The Cr(III) ion is situated on a crystallographic center. The symmetric unit of the title complex is consisted of half a Cr(III) complex anion and half

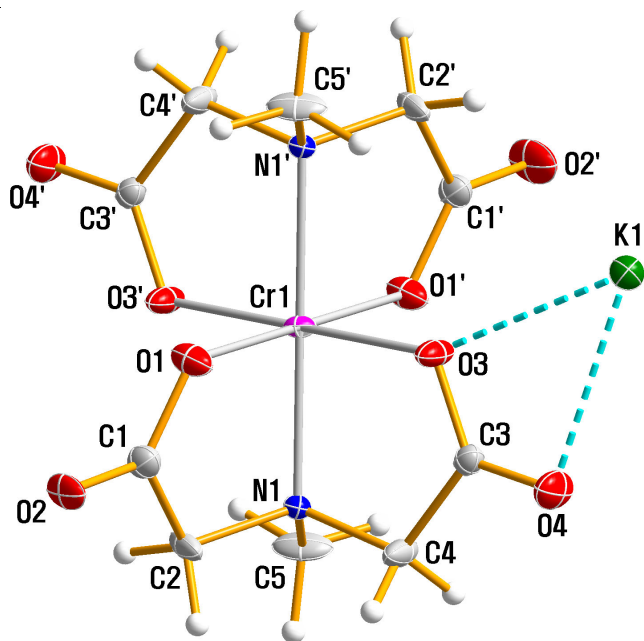


Fig. 2. The molecular structure of the title complex, showing the atom-numbering scheme. Non-H atoms are shown as displacement ellipsoids at the 70 % probability level. The primed atoms are related by symmetry code  $(-x+1, -y+1, -z+1)$ . Dashed lines represent K...O interactions

of one potassium cation. The Cr–O bond lengths of 1.9547 (12) and 1.9661 (12) Å agree with the corresponding values for  $\text{Na}[\text{Cr}(\text{mida})_2]$  and  $[(\text{NH}_4)_{0.8}\text{K}_{0.2}][\text{Cr}(\text{mida})_2]$  [3,4], but Cr–N bond lengths of 2.0740 (14) Å is slightly shorter than 2.118 Å ( $R = i\text{-C}_3\text{H}_7$ ) and 2.152 Å ( $R = \text{tert-C}_4\text{H}_9$ ) with more bigger sized substituent [5,6]. Bond angles about the central chromium atom are 90.57 (5)° for O1–Cr1–O3, 85.13 (6)° for O3–Cr1–N1 and 82.86 (5)° for O1–Cr1–N1 indicating a distorted octahedral coordination environment. The C–O bond lengths within the carboxylate group of the mida ligand range from 1.227 (2) to 1.2912 (19) Å and can be compared to values of 1.222 (3) and 1.283 (3) Å for  $\text{Na}[\text{Cr}(\text{mida})_2]$  [3]. The N–C and C–C distances in the mida moieties are close to the distances found in the free  $\text{H}_2\text{mida}$  molecule [17] and are equal to 1.402(3)–1.497(3) and 1.507(3)–1.514(3) Å, respectively. The potassium cation is connected in an irregular geometry by eight oxygen atoms of four acetate groups. The K–O distances lie in the range 2.7744(13)–2.931(13) Å.

The pattern around the cation is different from the crystal packing network in the related mixed ammonium/potassium salt [4]. The potassium cation is linked to the eight O atoms of carboxylate from neighbouring mida ligands through K...O. The crystal structure is stabilized by the H...O, H...H [18] and O...K interactions of the potassium cation and the O atoms of each mida ligand.

**Hirshfeld surface analysis:** The Hirshfeld-surface (HS) analysis allows for intuitive recognition and quantitative analysis of interactions between molecules [19]. The Hirshfeld-surface analysis has been performed by using CrystalExplorer17 [20]. The crystal packing diagrams along the b axis are shown in Fig. 3.

The  $d_{\text{norm}}$  surface shows the red and white spots indicating close contacts due to O...H, H...H and O...K interactions. 2-D

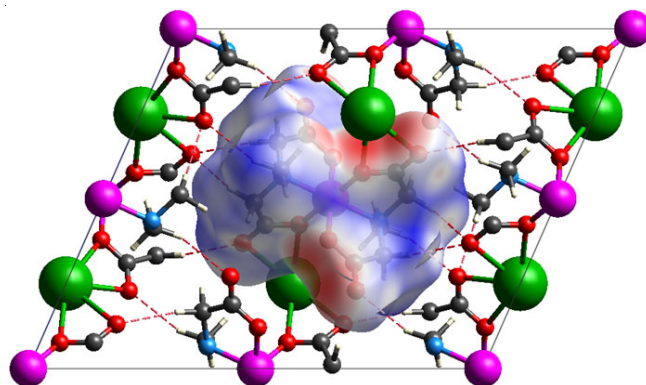


Fig. 3. Hirshfeld surface mapped with  $d_{\text{norm}}$  function and crystal packing of (I), viewed along the b axis. Dashed lines represent H...O contacts

fingerprint plot [21] of various interactions is shown in Fig. 4, where  $d_i$  is the closet internal distance from a given point on the Hirshfeld surface and  $d_e$  is the closest external contact, respectively [22]. The packing of the molecules is primarily driven by the O...H, H...H and O...K interactions. However, C...H, H...K, O...O and C...O contacts have little contributions of 3.8, 2.8, 2.7 and 1.4 %, respectively.

## Conclusion

It is confirmed that Cr(III) ion in the title complex was coordinated to two methyliminodiacetate (mida) dianions acting as tridentate ligands through the N atom and two O atoms of each carboxylate group in a distorted octahedral geometry. Two coordinated N atoms of mida ligands are mutually *trans* (*s-fac*) arrangement. The Cr–N bond length of 2.0740 (14) Å and two Cr–O bond lengths of 1.9547 (12) and 1.9661 (12) Å were observed. Hirshfeld surface analysis with 2D fingerprint plots showed that the O...H, H...H and O...K interactions are the main intermolecular interactions. The crystal structure is stabilized by the O...H, H...H and O...K interactions among potassium cation, H atoms and the O atoms of carboxylate group from neighbouring mida groups.

**Supplementary material:** Crystallographic data, tables of atomic coordinates and thermal parameters and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1534081. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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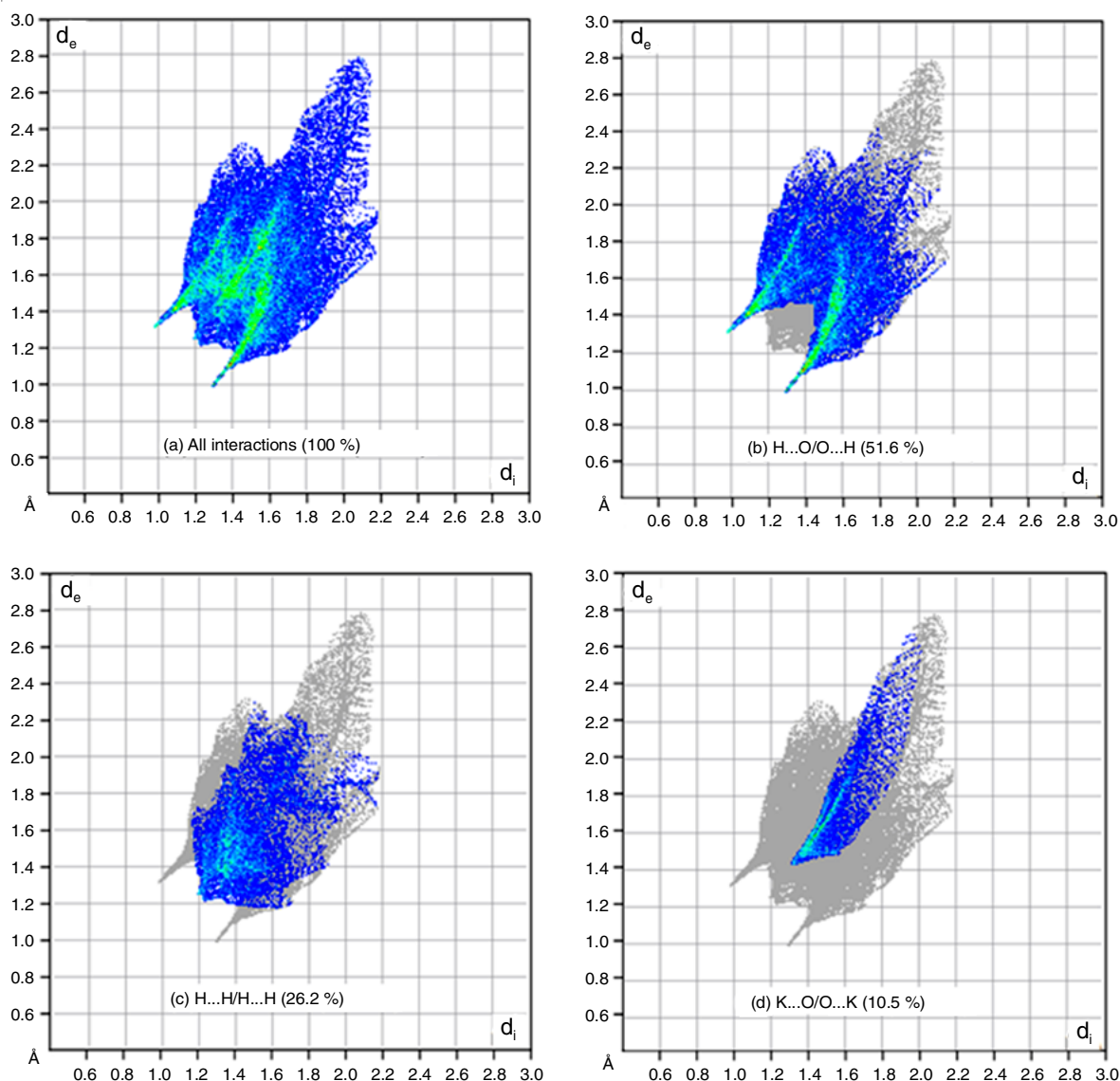


Fig. 4. Two-dimensional fingerprint plots of (I), corresponding to (a) all interactions, (b) O $\cdots$ H, (c) H $\cdots$ H and (d) O $\cdots$ K interactions

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