Crystal structure of potassium *trans*-diaquabis[oxalato-κ^2O,O] chromate(III) urea disolvate, $K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2CO(NH_2)_2$, $C_6H_{12}CrKN_4O_{12}$

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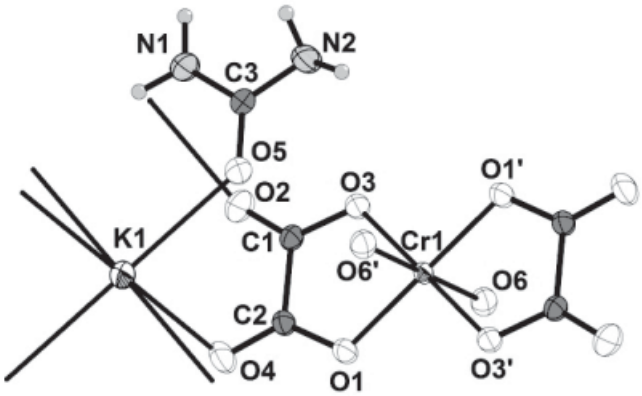

Abstract

$C_6H_{12}CrKN_4O_{12}$, triclinic, $P\bar{1}$ (No. 2), a = 5.101(1) Å, b = 7.029(1) Å, c = 10.554(2) Å, α = 76.73(3)°, β = 77.46(3)°, γ = 81.32(3)°, V = 357.5 Å^3, Z = 1, $R_{gt}(F)$ = 0.0321, $wR_{ref}(F^2)$ = 0.1327, T = 293 K.

Table 1. Data collection and handling.

Crystal:	violet blocks, size 0.10×0.15×0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.68 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD, integration method
$2\theta_{max}$:	56.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4370, 1722
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1579
$N(param)_{refined}$:	133
Programs:	SHELX [6]

Source of material

Commercially available $H_2C_2O_4\cdot 2H_2O$ (3.78 g, 30 mmol), and $CO(NH_2)_2$ (2.41 g, 40 mmol) were dissolved in H_2O (100mL) at 70ºC. The filtered solution was stirred at the same temperature and a powder of $K_2Cr_2O_7$ (2.97 g, 10 mmol, Riedel-de Haën) was added in successive small portions. Stirring was maintained for 1.5 hour. The bluish-violet reaction solution was then filtered and left to stand at room temperature. Violet brown single crystals suitable for X-ray diffraction were obtained after several days by slow evaporation of the solvent in 78% yield.

Experimental details

All non hydrogen atoms were treated anisotropically. All H atoms were located in a difference Fourier map and refined with following restraints: d(O–H) = 0.83(2) Å and d(N–H) = 0.90(2) Å. Their displacement parameters were refined freely but constrained to the same value for H atoms on the same heteroatom.

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Discussion

It is well known that transition metals coordinated by versatile multidentate ligands like oxalate anions affords various structural topologies [1-3]. The crystal structure of the title compound consists of anionic Cr^{III} complexes, $[Cr(C_2O_4)_2(H_2O)_2]^-$, K^+ cations and urea molecules.The asymetric unit is composed of all aforementioned species. The Cr^{III} ion in the complex anion, $[Cr(C_2O_4)_2(H_2O)_2]^-$ is six-coordinated in a slightly distorted octahedral coordination environment defined by two chelating bidentate oxalate anions in the equatorial plane and two aqua ligands in apical trans position (Fig.). The equatorial two pairs of Cr–O bond lengths are equal [1.964(2) and 1.969(2) Å] within standard deviation and slightly shorter than the apical Cr–O [2.0185(17) Å] pair. A similar coordination was previously observed in homologous salts involving quinolinium $(C_9H_8N)^+$ and 4-dimethylaminopyridium $(C_7H_{11}N_2)^+$ counter cations [4]. The K^+ cation is hexacoordinated by O atoms from four different oxalate anions in the equatorial plane and two urea molecules in trans position above the plane. This geometry is significantly different from what has been observed hitherto in $K[Cr(C_2O_4)_2(H_2O)_2]$ [5]. The K–O lengths vary within a range from 2.7037 (17) to 2.948 (2) Å and the pseudo orthogonal O–K–O angles vary in a range from 68.63(6) to 11.37(1)°. These angle values are in accordance with those previously reported [5]. Furthermore, the crystal structure is stabilized by intermolecular N–H···O and O–H···O hydrogen bonds.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(6A)	2*i*	0.31(1)	0.742(5)	0.497(2)	0.12(2)
H(6B)	2*i*	0.223(6)	0.885(4)	0.412(5)	0.12(2)
H(2A)	2*i*	0.222(8)	1.536(8)	0.601(4)	0.09(1)
H(2B)	2*i*	0.01(1)	1.612(5)	0.697(5)	0.09(1)
H(1B)	2*i*	–0.042(7)	1.310(4)	0.970(2)	0.030(5)
H(1A)	2*i*	–0.214(5)	1.468(4)	0.888(3)	0.030(5)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.1563(4)	0.9170(3)	0.7424(2)	0.018(1)	0.0230(9)	0.0171(9)	–0.0018(8)	–0.0008(7)	–0.0040(7)
C(2)	2*i*	0.4252(4)	0.7832(3)	0.7548(2)	0.019(1)	0.0225(9)	0.0163(9)	–0.0007(8)	–0.0027(7)	–0.0015(7)
O(1)	2*i*	0.5965(3)	0.7873(2)	0.6444(2)	0.0174(7)	0.0266(8)	0.0167(7)	0.0037(6)	–0.0022(6)	0.0000(6)
O(2)	2*i*	–0.0291(4)	0.9161(3)	0.8374(2)	0.0262(9)	0.0376(9)	0.0218(8)	0.0006(7)	0.0068(6)	–0.0040(7)
O(3)	2*i*	0.1526(3)	1.0230(2)	0.6236(1)	0.0160(7)	0.0266(7)	0.0165(7)	0.0022(6)	–0.0019(5)	–0.0023(6)
O(4)	2*i*	0.4612(4)	0.6866(3)	0.8633(2)	0.032(1)	0.0354(9)	0.0180(8)	0.0026(7)	–0.0046(7)	0.0043(6)
O(6)	2*i*	0.3536(3)	0.8094(2)	0.4233(2)	0.0177(7)	0.0276(8)	0.0190(7)	–0.0020(6)	–0.0028(6)	–0.0044(6)
Cr(1)	1*f*	$\frac{1}{2}$	1	$\frac{1}{2}$	0.0126(3)	0.0213(3)	0.0115(3)	0.0017(2)	–0.0015(2)	–0.0014(2)
K(1)	1*d*	$\frac{1}{2}$	1	1	0.0309(4)	0.0436(5)	0.0191(4)	0.0121(3)	–0.0030(3)	–0.0059(3)
C(3)	2*i*	0.1308(5)	1.3790(3)	0.7839(2)	0.026(1)	0.024(1)	0.020(1)	0.0019(8)	–0.0032(8)	–0.0067(8)
O(5)	2*i*	0.3478(3)	1.2692(3)	0.7911(2)	0.0230(8)	0.0346(9)	0.0206(8)	0.0068(7)	–0.0042(6)	–0.0067(6)
N(1)	2*i*	–0.0714(5)	1.3787(3)	0.8895(2)	0.028(1)	0.038(1)	0.024(1)	0.0068(9)	0.0028(8)	–0.0034(8)
N(2)	2*i*	0.0860(5)	1.4994(4)	0.6696(2)	0.030(1)	0.038(1)	0.025(1)	0.0076(9)	–0.0004(8)	0.0029(9)

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