Crystal structure of quinolinium *trans*-diaquabis(oxalato-*O*,*O'*)-chromate(III), $[C_9H_8N][Cr(H_2O)_2(C_2O_4)_2]$

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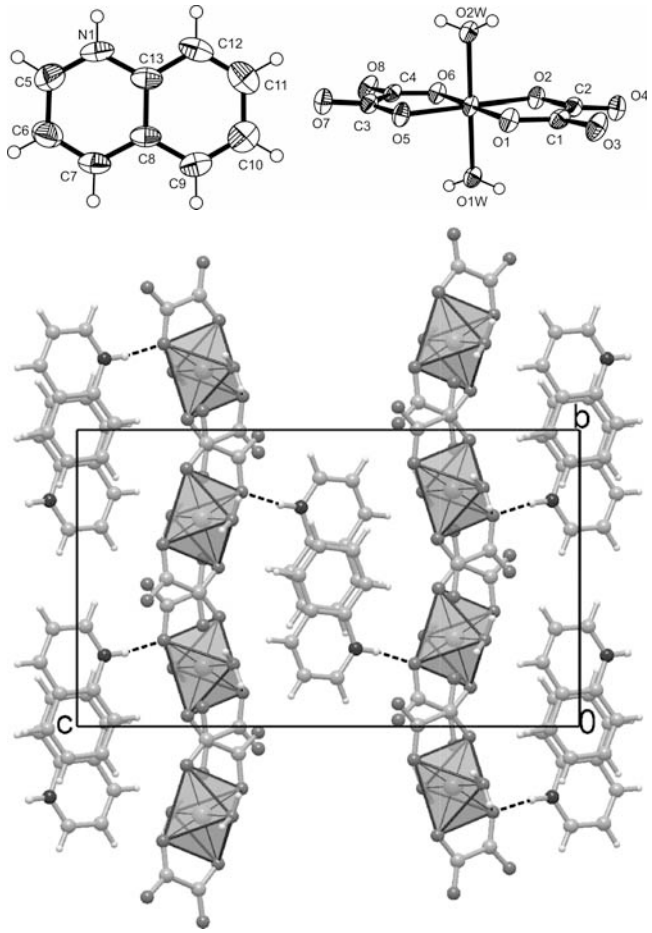

Abstract

$C_{13}H_{12}CrNO_{10}$, monoclinic, $P12_1/c1$ (no. 14), a = 7.541(1) Å, b = 10.936(2) Å, c = 18.594(3) Å, β = 94.261(3)°, V = 1529.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.115, T = 294 K.

Source of material

2 mmol (800 mg) of $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in 40 ml of water. The filtered solution was stirred at 318 K and 6.15 mmol (800 mg) of quinoline were added slowly, producing a green solution. 6.2 mmol (780 mg) of oxalic acid were added in successive small portions, the color of the mixture finally turned red-violet. After stirring another 1 h at same temperature, the filtered solution was slowly evaporated to complete dryness. The powder was dried in air. Recrystallization from water at room temperature yielded red-violet crystals used for X-ray diffraction. Elemental analysis — found: C, 39.32 %; H, 2.88 %; N, 3.42 %; calculated for $C_{13}H_{12}CrNO_{10}$: C, 39.61 %; H, 3.07 %; N, 3.55 %.

Experimental details

Hydrogen atoms were fixed at calculated positions and refined as riding at their parent atoms.

Discussion

The oxalate ion has recently moved into the focus of a considerable research activity around the world, due to its unique potential as a remarkably flexible ligand system in complexations with a wide range of metal ions [1]. In the past decades, many coordination compounds based on this ligand system were shown to play a crucial role in the rational design and development of novel materials that may combine, within a given system, a range of interesting solid state functionalities [2], such as molecular magnetism, optical activity, nano-channels in metal-organic frameworks (MOFs) [3], extended hydrogen-bonding. Such polyfunctional materials are needed to boost the advancement of the new millennium technologies.

The unit cell of the title salt contains four formula units, each of which consists of a quinolinium cation and a $[Cr(H_2O)_2(C_2O_4)_2]^-$ anion (figure, top). These discrete ions are stacked into segregated positive and negative layers parallel to (001), whereby the planar positive and the corrugated negative layers alternate along the [001] direction, being interconnected *via* N–H···O bridgings (d(N1···O1) = 2.887(4) Å) that link the quinolinium N–H groups to the coordinated oxalato O atoms (dashed lines, figure, bottom). The quinolinium stacks are centered on a 2-fold axis which extends throughout the lattice across the centers of the superimposed benzenic ring systems, in eclipsed configuration and 3.77 Å apart, revealing weak π-π interactions within these stacks. The cations and the main planes of the complex anions of this salt are disposed in a fish-bone fashion, defining the respective dihedral angles of 63.50° and 56.91° with respect to (001). The bond lengths and angles within the quinolinium cation are in accord with reported values [4]. The complex anions contain Cr(III) centers in a prolate (4+2) octahedral coordination of two chelating, equatorial oxalato ligands and two axial water molecules, the equatorial Cr—O bond lengths ranging from 1.955(1) to 1.976(1) Å, and the axial Cr—O distances being virtually identical at 2.000(2) and 2.002(2) Å. The shortest intralayer Cr-Cr spacing is d(Cr-Cr) = 6.635(1) Å.

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Table 1. Data collection and handling.

Crystal:	red block, size 0.1 × 0.15 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	8.06 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω
$2\theta_{max}$:	54.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9872, 3343
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2477
$N(param)_{refined}$:	226
Programs:	SHELXS-97 [5], SHELXL-97 [6], SHELXTL [7], ORTEP-III [8]

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

Atom	Site	x	y	z	U_{iso}
H(11)	4*e*	0.5540	0.2499	0.2048	0.042
H(12)	4*e*	0.4980	0.3631	0.1741	0.042
H(21)	4*e*	–0.0494	0.3405	0.2883	0.042
H(22)	4*e*	0.0045	0.2350	0.3206	0.042
H(1)	4*e*	0.4159	0.7525	0.0949	0.058
H(9)	4*e*	0.1016	1.0194	–0.1033	0.055
H(12A)	4*e*	0.4222	0.9707	0.1187	0.060
H(7)	4*e*	0.0928	0.7908	–0.1175	0.056
H(11A)	4*e*	0.3458	1.1604	0.0769	0.069
H(6)	4*e*	0.1730	0.6023	–0.0740	0.068
H(10)	4*e*	0.1825	1.1855	–0.0347	0.066
H(5)	4*e*	0.3407	0.5867	0.0348	0.068

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}
Cr(1)	4*e*	0.25062(4)	0.29847(3)	0.24856(2)	0.0190(2)	0.0169(2)	0.0293(2)	–0.0004(1)	–0.0047(1)	–0.0013(1)
O(1)	4*e*	0.1844(2)	0.1319(1)	0.21775(8)	0.0254(8)	0.0217(8)	0.0346(8)	–0.0012(6)	–0.0062(6)	–0.0035(6)
O(2)	4*e*	0.3863(2)	0.2101(1)	0.32734(8)	0.0272(8)	0.0204(8)	0.0322(8)	–0.0001(6)	–0.0059(6)	–0.0016(6)
O(3)	4*e*	0.2335(2)	–0.0637(2)	0.24938(9)	0.0295(9)	0.0173(8)	0.057(1)	–0.0023(6)	–0.0036(7)	–0.0047(7)
O(4)	4*e*	0.4671(2)	0.0208(1)	0.36024(8)	0.0350(9)	0.0273(9)	0.0378(9)	0.0057(7)	–0.0059(7)	0.0026(7)
O(5)	4*e*	0.1180(2)	0.3873(1)	0.17078(8)	0.0278(8)	0.0209(8)	0.0341(8)	0.0011(6)	–0.0074(6)	–0.0014(7)
O(6)	4*e*	0.3180(2)	0.4642(1)	0.28040(8)	0.0254(8)	0.0212(8)	0.0343(9)	–0.0013(6)	–0.0049(6)	–0.0031(6)
O(7)	4*e*	0.0308(2)	0.5763(2)	0.13948(9)	0.0391(9)	0.0281(9)	0.0392(9)	0.0060(7)	–0.0053(7)	0.0036(7)
O(8)	4*e*	0.2676(2)	0.6595(2)	0.25021(9)	0.0299(9)	0.0179(8)	0.062(1)	–0.0007(6)	–0.0044(8)	–0.0057(7)
O(1W)	4*e*	0.4609(2)	0.2910(1)	0.18904(8)	0.0222(8)	0.0228(8)	0.0382(9)	–0.0002(6)	–0.0001(6)	0.0004(6)
O(2W)	4*e*	0.0404(2)	0.3038(1)	0.30808(8)	0.0216(8)	0.0217(8)	0.0394(9)	–0.0009(6)	–0.0017(6)	0.0009(6)
C(1)	4*e*	0.2554(2)	0.0466(2)	0.2572(1)	0.016(1)	0.025(1)	0.035(1)	–0.0016(8)	0.0020(8)	–0.0024(9)
C(2)	4*e*	0.3815(3)	0.0926(2)	0.3211(1)	0.023(1)	0.024(1)	0.030(1)	0.0003(9)	0.0025(8)	0.0007(9)
C(3)	4*e*	0.1190(3)	0.5034(2)	0.1778(1)	0.022(1)	0.023(1)	0.030(1)	0.0005(8)	0.0018(8)	0.0006(9)
C(4)	4*e*	0.2448(2)	0.5500(2)	0.2416(1)	0.018(1)	0.022(1)	0.036(1)	–0.0005(8)	0.0030(8)	–0.0028(9)
N(1)	4*e*	0.3535(3)	0.7615(2)	0.0546(1)	0.039(1)	0.070(2)	0.035(1)	0.008(1)	–0.0088(9)	0.010(1)
C(9)	4*e*	0.1648(3)	1.0088(3)	–0.0589(1)	0.038(1)	0.062(2)	0.038(1)	0.004(1)	0.003(1)	0.010(1)
C(13)	4*e*	0.3078(3)	0.8778(3)	0.0324(1)	0.027(1)	0.064(2)	0.030(1)	0.001(1)	0.0021(9)	0.001(1)
C(12)	4*e*	0.3581(3)	0.9800(3)	0.0744(1)	0.040(2)	0.077(2)	0.033(1)	–0.007(1)	0.000(1)	–0.008(1)
C(8)	4*e*	0.2090(3)	0.8903(3)	–0.0345(1)	0.026(1)	0.060(2)	0.028(1)	0.002(1)	0.0007(9)	0.002(1)
C(7)	4*e*	0.1593(3)	0.7840(3)	–0.0736(1)	0.037(1)	0.068(2)	0.034(1)	0.004(1)	–0.007(1)	–0.002(1)
C(11)	4*e*	0.3124(4)	1.0920(3)	0.0495(2)	0.052(2)	0.066(2)	0.055(2)	–0.013(2)	0.013(1)	–0.015(2)
C(6)	4*e*	0.2068(4)	0.6722(3)	–0.0480(2)	0.052(2)	0.064(2)	0.052(2)	0.006(2)	–0.011(1)	–0.012(2)
C(10)	4*e*	0.2135(4)	1.1075(3)	–0.0184(2)	0.048(2)	0.060(2)	0.059(2)	0.001(1)	0.012(1)	0.007(2)
C(5)	4*e*	0.3064(4)	0.6633(3)	0.0171(2)	0.053(2)	0.056(2)	0.059(2)	0.008(2)	–0.007(1)	0.006(2)

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