Crystal structure of tris[*N,N*-bis(2-hydroxyethyl)-dithiocarbamato- κ^2S,S']-chromium(III), $C_{15}H_{30}CrN_3O_6S_6$

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Received December 16, 2013, accepted January 17, 2014, available online January 28, 2014, CCDC no. 983023

Abstract

$C_{15}H_{30}CrN_3O_6S_6$, monoclinic, Cc (no. 9), $a = 17.704(4)$ Å, $b = 10.314(2)$ Å, $c = 14.154(3)$ Å, $\beta = 112.40(3)^\circ$, $V = 2389.6$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0383$, $wR_{\text{ref}}(F^2) = 0.0996$, $T = 100$ K.

Table 1. Data collection and handling.

Crystal:	purple blocks, size 0.11×0.12×0.15 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	10.41 cm ⁻¹
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	10212, 5230
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4887
$N(\text{param})_{\text{refined}}$:	305
Programs:	SADABS [8], SAINT [8], SHELX [9], ORTEP-3 [10]

Source of material

Chromium chloride hexahydrate (1.029 g, 5.061 mmol) and potassium di(*N*-hydroxyethyl)dithiocarbamate were each dissolved separately in ethanol (50 ml). The ethanolic solution of the latter was stirred, the chromium chloride solution was added to it dropwise, and the solution turned purple. The solution was filtered and crystals form after a few days of slow evaporation under ambient conditions.

Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.99$ Å) and refined as riding with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. The hydroxy-H atoms were refined with the distance constraint $O-H = 0.84 \pm 0.01$ Å, and with unrestrained $U_{\text{iso}}(H)$. Two reflections, *i.e.*

(4 0 0) and (-4 0 0) were omitted from the final cycles of refinement owing to poor agreement. The sample is a racemic twin (2494 Friedel pairs) precluding the determination of the absolute structure.

Discussion

As a continuation of studies into the supramolecular aggregation patterns of metal complexes containing functionalised dithiocarbamate ligands, in particular having hydroxyethyl groups [1–4], the structure of $Cr[S_2CN(CH_2CH_2OH)_2]_3$ was studied. The Cr(III) atom exists in a distorted octahedral geometry defined by three chelating ligands which form symmetric Cr–S bond lengths which span a narrow range of 2.3734(10) to 2.3937(13) Å. Reflecting this symmetric mode of coordination, the associated C–S bond lengths are experimentally equivalent (range: 1.715(4) to 1.730(4) Å). The twist between the trigonal face comprising the more tightly bound sulphur atoms (S1, S3 and S5) and the other face is ca. 42°, indicating a significant distortion toward a trigonal prismatic coordination geometry. This observation reflects the influence of the restricted bite angles of the ligands (range: 74.06(4) to 74.42(3)°). As anticipated from the chemical composition, significant hydrogen bonding features in the crystal packing. Thus, O–H⋯O, S hydrogen bonding stabilise the molecules into a three-dimensional architecture. The molecule is close to having crystallographic two-fold symmetry. However, small but experimentally significant differences in Cr–S bond lengths for all three ligands ($\Delta(Cr-S) = 0.08$ –0.12 Å) and the hydrogen bonding pattern precludes the higher symmetry. The molecular structure reported herein resembles literature precedents for $Cr(S_2CNR_2)_3$, having alkyl substituents, *e.g.* R = Et [5] and CH_2Ph [6].

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
H(1O)	4a	0.705(3)	0.219(4)	0.786(3)	0.04(2)
H(2O)	4a	0.732(4)	0.483(3)	0.401(5)	0.06(2)
H(3O)	4a	0.612(2)	0.938(4)	0.815(3)	0.03(1)
H(4O)	4a	0.411(2)	1.235(2)	0.484(3)	0.013(9)
H(5O)	4a	0.271(1)	0.174(5)	0.444(3)	0.05(2)
H(6O)	4a	0.192(3)	0.486(1)	0.742(4)	0.04(1)
H(2A)	4a	0.7496	0.4071	0.7033	0.019
H(2B)	4a	0.7881	0.3560	0.6245	0.019

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Table 2. continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(3A)	4a	0.7733	0.1416	0.6628	0.022
H(3B)	4a	0.8165	0.2149	0.7696	0.022
H(4A)	4a	0.6031	0.2177	0.4537	0.019
H(4B)	4a	0.7001	0.1978	0.4955	0.019
H(5A)	4a	0.6496	0.2993	0.3321	0.021
H(5B)	4a	0.6181	0.4190	0.3796	0.021
H(7A)	4a	0.4297	0.9573	0.7213	0.019
H(7B)	4a	0.4218	1.0876	0.6572	0.019
H(8A)	4a	0.5648	1.1229	0.7476	0.023
H(8B)	4a	0.5127	1.1302	0.8183	0.023
H(9A)	4a	0.5350	0.9679	0.5146	0.020

Table 2. continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(9B)	4a	0.5339	1.0963	0.5772	0.020
H(10A)	4a	0.4459	1.1067	0.3990	0.022
H(10B)	4a	0.3903	0.9968	0.4199	0.022
H(12A)	4a	0.1872	0.3981	0.4868	0.018
H(12B)	4a	0.1514	0.3348	0.5643	0.018
H(13A)	4a	0.1896	0.1240	0.5202	0.022
H(13B)	4a	0.1168	0.1931	0.4293	0.022
H(14A)	4a	0.3391	0.2153	0.7375	0.018
H(14B)	4a	0.2430	0.1866	0.6936	0.018
H(15A)	4a	0.2827	0.2984	0.8520	0.021
H(15B)	4a	0.3171	0.4160	0.8059	0.021

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cr	4a	0.46780(4)	0.54022(4)	0.59279(4)	0.0090(2)	0.0118(2)	0.0132(2)	−0.0007(3)	0.0050(2)	−0.0004(2)
S(1)	4a	0.61023(5)	0.50057(8)	0.67993(6)	0.0121(4)	0.0184(4)	0.0154(4)	0.0000(3)	0.0048(3)	−0.0040(3)
S(2)	4a	0.50626(5)	0.40088(8)	0.48370(6)	0.0108(4)	0.0173(4)	0.0149(4)	−0.0004(3)	0.0032(3)	−0.0017(3)
S(3)	4a	0.45806(5)	0.71689(8)	0.69500(6)	0.0152(4)	0.0156(4)	0.0175(4)	0.0001(3)	0.0087(3)	−0.0001(3)
S(4)	4a	0.47911(5)	0.73058(8)	0.50345(6)	0.0152(4)	0.0161(4)	0.0173(4)	−0.0002(3)	0.0085(3)	−0.0001(3)
S(5)	4a	0.43397(5)	0.38783(8)	0.69689(6)	0.0113(4)	0.0166(4)	0.0156(4)	−0.0003(3)	0.0031(3)	0.0024(3)
S(6)	4a	0.32553(5)	0.49390(8)	0.50512(6)	0.0124(4)	0.0165(4)	0.0146(4)	0.0005(3)	0.0048(4)	0.0027(3)
N(1)	4a	0.6654(2)	0.3389(3)	0.5717(2)	0.011(1)	0.013(1)	0.014(1)	0.000(1)	0.005(1)	−0.001(1)
N(2)	4a	0.4792(2)	0.9430(2)	0.6143(2)	0.013(1)	0.015(1)	0.014(2)	−0.001(1)	0.006(1)	0.001(1)
N(3)	4a	0.2750(2)	0.3250(3)	0.6147(2)	0.013(2)	0.014(1)	0.014(1)	−0.002(1)	0.005(1)	−0.001(1)
O(1)	4a	0.7015(2)	0.1659(2)	0.7398(2)	0.018(1)	0.022(1)	0.022(1)	0.000(1)	0.010(1)	0.002(1)
O(2)	4a	0.7397(2)	0.4087(3)	0.4274(2)	0.019(1)	0.024(1)	0.025(2)	−0.005(1)	0.010(1)	0.001(1)
O(3)	4a	0.5830(2)	0.9751(2)	0.8425(2)	0.018(1)	0.025(1)	0.018(1)	0.003(1)	0.005(1)	0.002(1)
O(4)	4a	0.3839(2)	1.1676(2)	0.4822(2)	0.018(1)	0.018(1)	0.029(1)	0.001(1)	0.009(1)	0.000(1)
O(5)	4a	0.2216(2)	0.1873(3)	0.4076(2)	0.013(1)	0.027(1)	0.017(1)	−0.001(1)	0.005(1)	−0.004(1)
O(6)	4a	0.1953(2)	0.4051(2)	0.7500(2)	0.016(1)	0.020(1)	0.025(1)	0.001(1)	0.010(1)	−0.001(1)
C(1)	4a	0.6028(2)	0.4028(3)	0.5787(3)	0.013(2)	0.012(1)	0.015(2)	−0.001(1)	0.005(1)	0.002(1)
C(2)	4a	0.7464(2)	0.3377(3)	0.6536(3)	0.011(2)	0.020(2)	0.017(2)	0.001(1)	0.005(1)	0.002(1)
C(3)	4a	0.7651(2)	0.2077(4)	0.7087(3)	0.016(2)	0.024(2)	0.016(2)	0.003(1)	0.008(2)	0.002(1)
C(4)	4a	0.6562(2)	0.2637(3)	0.4784(3)	0.017(2)	0.016(2)	0.015(2)	0.001(1)	0.006(2)	−0.002(1)
C(5)	4a	0.6603(2)	0.3505(3)	0.3950(3)	0.019(2)	0.018(2)	0.019(2)	0.000(1)	0.009(2)	−0.001(1)
C(6)	4a	0.4723(3)	0.8155(3)	0.6054(3)	0.009(1)	0.020(1)	0.018(2)	0.004(2)	0.005(1)	0.001(1)
C(7)	4a	0.4592(2)	1.0157(3)	0.6916(3)	0.013(2)	0.016(1)	0.019(2)	0.002(1)	0.006(1)	−0.003(1)
C(8)	4a	0.5321(2)	1.0710(3)	0.7772(3)	0.020(2)	0.016(1)	0.022(2)	0.000(1)	0.010(2)	−0.000(1)
C(9)	4a	0.5008(2)	1.0211(3)	0.5409(3)	0.014(2)	0.016(1)	0.025(2)	0.003(1)	0.011(2)	0.006(1)
C(10)	4a	0.4274(2)	1.0702(3)	0.4512(3)	0.018(2)	0.017(2)	0.020(2)	−0.002(1)	0.007(2)	−0.001(1)
C(11)	4a	0.3362(2)	0.3926(3)	0.6068(3)	0.016(2)	0.013(2)	0.014(2)	0.001(1)	0.006(2)	−0.002(1)
C(12)	4a	0.1926(2)	0.3240(3)	0.5334(3)	0.007(2)	0.020(2)	0.017(2)	−0.001(1)	0.003(1)	−0.001(1)
C(13)	4a	0.1759(2)	0.1982(4)	0.4722(3)	0.015(2)	0.021(2)	0.019(2)	−0.004(2)	0.006(2)	−0.002(2)
C(14)	4a	0.2845(2)	0.2562(3)	0.7092(3)	0.015(2)	0.014(1)	0.019(2)	−0.002(1)	0.008(2)	0.002(1)
C(15)	4a	0.2749(2)	0.3474(4)	0.7888(3)	0.012(2)	0.025(2)	0.016(2)	−0.002(2)	0.005(1)	0.001(1)

Acknowledgments. Support from the University of Malaya Research Grants scheme (RG166/11AFR) is gratefully acknowledged. We also acknowledge support for the publication fee by the Institut Pengurusan dan Pemantauan Penyelidikan (IPPP) of the University of Malaya.

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