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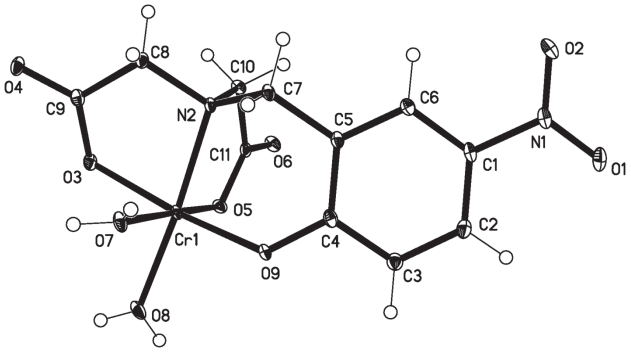
The crystal structure of diaqua-(*N*-(2-hydroxy-5-nitrobenzyl)iminodiacetato-κ^4-*N*,*O*,*O*′,*O*″) chromium(III) based on synchrotron data, $C_{11}H_{13}CrN_2O_9$



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Abstract

$C_{11}H_{13}CrN_2O_9$, orthorhombic, *Pbca* (no. 61), $a = 6.7740(14)$ Å, $b = 12.309(3)$ Å, $c = 32.776(7)$ Å, $V = 2732.9(10)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0302$, $wR_{ref}(F^2) = 0.0867$, $T = 100(2)$ K.

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Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

To an aqueous solution (80 mL) containing iminodiacetic acid (8.35 g, 0.0625 mol) and *p*-nitrophenol (8.688 g, 0.0625 mol) cooled in an ice-water bath was added NaOH

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Table 1: Data collection and handling.

Crystal:	Green, blocks Size 0.10 × 0.08 × 0.05 mm
Wavelength:	Sychrotron radiation (0.7200 Å)
μ:	8.9 cm^{-1}
Diffractometer, scan mode:	MAR-CCD-165, ω
$2\theta_{max}$, completeness:	61.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7898, 2376, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2164
$N(param)_{refined}$:	210
Programs:	Data reduction programs [8, 9], SHELX [10]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cr1	0.17385(5)	0.97311(2)	0.821006(8)	0.00980(13)
O5	0.3296(2)	0.84285(11)	0.82770(4)	0.0134(3)
O3	0.3666(2)	1.02975(10)	0.77982(4)	0.0136(3)
N2	0.3811(3)	1.04153(13)	0.85929(5)	0.0100(3)
C5	0.1975(3)	0.98350(16)	0.92196(6)	0.0119(4)
O9	0.0018(2)	0.93260(12)	0.86424(4)	0.0145(3)
C7	0.2886(3)	1.07681(16)	0.89893(6)	0.0118(4)
H7A	0.3886	1.1107	0.9159	0.014*
H7B	0.1877	1.1307	0.8933	0.014*
O6	0.5920(2)	0.76868(11)	0.85736(4)	0.0163(3)
C11	0.4866(3)	0.84806(16)	0.84984(6)	0.0122(4)
C9	0.4589(3)	1.11660(16)	0.79143(6)	0.0130(4)
C6	0.2397(3)	0.96875(16)	0.96297(6)	0.0135(4)
H6	0.3373	1.0100	0.9756	0.016*
C8	0.4584(3)	1.13873(16)	0.83703(5)	0.0125(4)
H8A	0.5915	1.1547	0.8461	0.015*
H8B	0.3761	1.2013	0.8429	0.015*
C10	0.5421(3)	0.95925(16)	0.86618(6)	0.0125(4)
H10A	0.5688	0.9537	0.8952	0.015*
H10B	0.6619	0.9838	0.8528	0.015*
C3	−0.0507(3)	0.84005(16)	0.92625(6)	0.0155(4)
H3	−0.1457	0.7965	0.9139	0.019*
C4	0.0509(3)	0.91849(17)	0.90304(6)	0.0132(4)
O4	0.5401(2)	1.18057(11)	0.76768(4)	0.0164(3)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
O7	0.0139(2)	1.10655(11)	0.81058(4)	0.0145(3)
H7C	0.0309	1.1266	0.7870	0.022*
O8	0.0081(2)	0.89848(11)	0.77878(4)	0.0191(3)
H8C	−0.0410	0.9440	0.7636	0.029*
O2	0.3042(2)	0.93528(14)	1.04410(4)	0.0225(4)
N1	0.1713(3)	0.88046(15)	1.02866(5)	0.0163(4)
C1	0.1346(3)	0.89165(17)	0.98507(6)	0.0144(4)
C2	−0.0097(3)	0.82760(17)	0.96720(6)	0.0163(4)
H2	−0.0782	0.7767	0.9827	0.020*
O1	0.0693(2)	0.81645(13)	1.04833(4)	0.0221(4)
H7D	−0.0246	1.1494	0.8250	0.033*
H8D	−0.0202	0.8260	0.7775	0.033*

(5.25 g, 0.125 mol) in water (20 mL). Formaldehyde (7.5 mL, 37%) was then added dropwise at 273 K. The solution was stirred for 30 min, heated at 343 K for 4 h and then evaporated to dryness. Recrystallization of the solid from methanol yielded yellow crystals of $[Na_2(NO_2\text{-}HXDA)]\cdot 2H_2O$ (yield 90%). Elemental analysis for $C_{11}H_{14}N_2Na_2O_9$: calc. C 36.27; H 3.87; N 7.69; Found: C 35.75; H 3.90; N 7.69. IR (KBr pellet) ν/cm^{-1}: 3437, 2932, 2359, 1630, 1406, 1302, 1161, 914. For the synthesis of the title compound, $Cr_2(SO_4)_3\cdot 6H_2O$ (0.2 mmol, 0.1057 g) and sodium (*N*-(2-hydroxy-5-nitrobenzyl)iminodiacetate (0.2 mmol, 0.1038 g) were dissolved separately in water (2 × 5 mL), mixed and stirred at 323 K for 24 h. The resulting crimson solution was filtered and the filtrate left to stand at room temperature. Pale violet crystals of the title compound appeared after 10 days by slow evaporation in 10% yield. Elemental analysis for $C_{11}H_{13}CrN_2O_9$: calc. C 35.78; H 3.55; N 7.59; Found: C 35.95; H 3.62; N 7.68.

Experimental details

Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C—O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [10]), with U_{iso}(H) set to 1.5U_{eq}(O).

Discussion

There is a compelling interest in the synthesis and characterization of transition metal complexes with pincer ligands for the wide range of studies from catalysis to bioinorganic and materials chemistry [1–3]. R—H_3XD′S [N-(2-hydroxy-5-R-benzyl)iminodiacetic acids with R = CH_3, Cl, Br, OMe, and NO_2 etc], are versatile acidic pincer ligands, which have one chelating arms like a single arm crab. They provide a convenient mononucleating feature with the phenolate oxygen and the $RN(CH_2COOH)_2$ arm, and have been used to incorporate various mono- or dinuclear cores [4, 5]. Recently, we synthetized the ligand NO_2-H_3XDA [N-(2-hydroxy-5-nitrobenzyl)iminodiacetic acid], and obtained the title pincer complex. Although they are the interesting organic electron and hydrogen transfer systems, the examples documented in the CSD of structurally characterized NO_2-H_3XDA metal compounds are only two hits: the mononuclear copper [6] and gallium [7] complexes. Moreover, due to the characteristics of these carboxylate-rich complexes hydrogen bonds can be found.

The asymmetric unit of the title structure consisted of a Cr(III) ion, one L^{3-} and two coordinated water molecules, in which the ligand anions had ‘single organic arm’ to chelate only one chromium ion. (*cf*. the figure). Bond lengths and angles in the ligand are in the expected ranges. The Cr(III) shows a slightly distorted octahedral coordination geometry, consisted of two carboxylate O atoms, a tertiary N atom, two water molecules and the phenolic O atom. The bond lengths of Cr—O ranging from 1.901(2) to 2.005(2) Å and Cr—N is 2.062(2) Å. The axial and equatorial plane angles O—Cr—O, N—Cr—O are ranging from 79.87(7) and 97.91(6)°, while the axials angles falling in a range between 171.15(7) and 176.66(6)°. According to the similar ionic radius, both bond lengths and angles are unremarkable compared to the documented mononuclear NO_2-H_3XDA complexes of Cu(II) [6] and Ga(III) [7].

Adjacent complexes are connected via NH···O and OH···H hydrogen bonds.

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