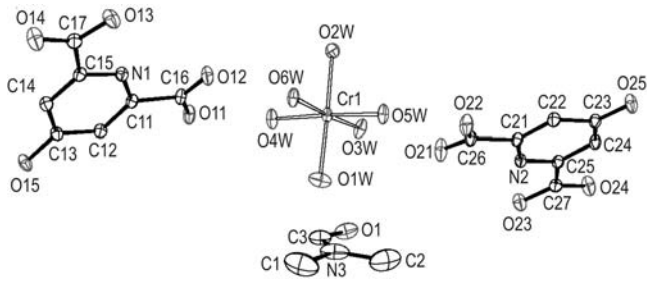
Crystal structure of hexaaquachromium(III) dimethylformamidium bis(4-hydroxypyridine-2,6-dicarboxylate), $[Cr(H_2O)_6][C_3H_8NO][C_7H_3NO_5]_2$

Qiu-Ju Xing, Shun-Chen Dai, Mei-Hong Chen, Jun Ma, Lu-Ping Zhang and Jian-Ping Zou*

Nanchang Hangkong University, School of Environmental and Chemical Engineering, Nanchang 330063, Jiangxi, P. R. China

Received November 12, 2010, accepted and available on-line December 6, 2010; CCDC no. 1267/3283



Abstract

$C_{17}H_{26}CrN_3O_{17}$, monoclinic, $P12_1/c1$ (no. 14), a = 17.7554(8) Å, b = 7.5999(4) Å, c = 22.1542(8) Å, β = 124.248(3)°, V = 2471.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.156, T = 293 K.

Source of material

A mixture of chromium(III) nitrate (0.03 mmol, 0.013 g), and chelidamic acid (0.11 mmol, 0.02 g) were dissolved in a 10 mL water. After slow adding 1 mL ethanol and 5 mL DMF, adjusting pH to 5, stirring for about 4 h, the mixed solution was filtered. The filtrate was allowed to stand at room temperature. Green prism-shaped crystals that are stable in air were obtained over a period of 10 d. Elemental analysis — found: C, 34.28 %; H, 3.73 %; N, 7.10 %; calculated for $C_{17}H_{25}CrN_3O_{17}$: C, 34.23 %; H, 3.69 %; N, 7.04 %.

Experimental details

All the H atoms of water molecules were found in difference Fourier map and refined with U_{iso}(H) = 1.5 U_{eq}(O). Other H atoms (except for O25) were all placed in calculated positions and allowed to ride on its parent atoms with d(C—H) = 0.96 Å, d(N—H) = 0.86 Å, d(O—H) = 0.82 Å, and U_{iso}(H) = 1.5 U_{eq}(C), U_{iso}(H) = 1.2 U_{eq}(N), U_{iso}(H) = 1.2 U_{eq}(O), respectively.

Discussion

The asymmetrical unit of the title crystal structure consists of one Cr atom, two discret chelidamic acid ligands, six coordinating water molecules and one discret *N*,*N*-dimethylformamide (DMF) molecules. The Cr(III) ion is coordinated by six water molecules to form a distorted octahedron. The equatorial plane consists of four oxygen atoms (O3W, O4W, O5W and O6W), while the axial positions are occupied by another two water oxygenss (O1W and O2W). The bond lengths of Cr—O range from 1.934(2) to 1.981(2) Å, which falls in the normal range reported for the chromium complexes in the literature [1-4]. The discret chromium complexes in the title compound are linked by the hydrogen bonds between O1W and O11, O2W and O25, O1 and O2W, O3W and O13, O4W and O14, O5W and O24, O6W and O23 to form an infinite chain along the [001]. The neighboring chains are connected into a layer through the hydrogen bonds between O1 and O1W, O15 and O25. These layers are in turn inter-linked through a very complex hydrogen bonding network involving water molecules and oxygen atoms from the chelidamic acid ligands to form a 3D supramolecular network. The chromium atoms and the chelidamate anions show oxidation states of +3 and –2, respectively. Thus, for charge neutralization, the discret DMF molecule should protonated through locating the H atom on N3 or O1 atoms. But we could not locate the hydrogen atoms in the difference Fourier map.

Table 1. Data collection and handling.

Crystal:	green prism, size 0.16 × 0.24 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.51 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22384, 6082
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4916
$N(param)_{refined}$:	379
Programs:	SHELXS-97, SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1WA)	4*e*	0.127(2)	0.198(4)	0.272(2)	0.068
H(1WB)	4*e*	0.204(2)	0.183(4)	0.340(2)	0.068
H(2WA)	4*e*	0.240(2)	0.817(4)	0.331(1)	0.048
H(2WB)	4*e*	0.260(2)	0.786(4)	0.282(2)	0.048
H(3WA)	4*e*	0.160(2)	0.520(4)	0.174(2)	0.051
H(3WB)	4*e*	0.237(2)	0.419(4)	0.208(2)	0.051
H(4WA)	4*e*	0.045(2)	0.602(4)	0.204(1)	0.050
H(4WB)	4*e*	0.048(2)	0.595(4)	0.264(2)	0.050
H(5WA)	4*e*	0.362(2)	0.396(4)	0.344(1)	0.046
H(5WB)	4*e*	0.364(2)	0.387(4)	0.400(1)	0.046
H(6WA)	4*e*	0.177(2)	0.590(4)	0.399(2)	0.044
H(6WB)	4*e*	0.249(2)	0.478(3)	0.429(2)	0.044
H(15A)	4*e*	–0.2684	0.4496	0.3369	0.049
H(1A)	4*e*	0.2410	–0.0950	0.5480	0.150
H(1B)	4*e*	0.3457	–0.1044	0.6087	0.150
H(1C)	4*e*	0.2933	–0.2736	0.5643	0.150
H(2A)	4*e*	0.4042	–0.1344	0.4790	0.136
H(2B)	4*e*	0.4007	–0.2988	0.5200	0.136

* Correspondence author (e-mail: zjp_112@126.com)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2C)	4*e*	0.4524	–0.1286	0.5639	0.136
H(3A)	4*e*	0.2041	0.0206	0.4432	0.055
H(12A)	4*e*	–0.1536	0.5103	0.3209	0.028
H(14A)	4*e*	–0.1568	0.6626	0.4949	0.030
H(22A)	4*e*	0.5743	0.3890	0.2992	0.031
H(24A)	4*e*	0.5681	0.2679	0.1184	0.033

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*	0.20387(2)	0.50138(4)	0.30247(2)	0.0179(2)	0.0285(2)	0.0151(2)	0.0053(1)	0.0100(2)	0.0053(1)
O(1W)	4*e*	0.1751(1)	0.2535(2)	0.3053(1)	0.0396(9)	0.0346(9)	0.0300(9)	–0.0065(7)	0.0001(7)	0.0101(7)
O(1)	4*e*	0.2661(1)	0.0033(2)	0.3979(1)	0.072(1)	0.034(1)	0.032(1)	0.0047(7)	0.023(1)	0.0058(7)
O(2W)	4*e*	0.2281(1)	0.7532(2)	0.29711(9)	0.0409(8)	0.0326(8)	0.0358(9)	0.0004(6)	0.0292(7)	0.0043(6)
O(3W)	4*e*	0.1936(1)	0.4648(2)	0.21170(8)	0.0337(8)	0.0518(9)	0.0191(7)	0.0212(7)	0.0163(7)	0.0099(7)
O(4W)	4*e*	0.07176(9)	0.5491(2)	0.24456(8)	0.0209(7)	0.061(1)	0.0211(7)	0.0121(7)	0.0133(6)	0.0139(7)
O(5W)	4*e*	0.33449(9)	0.4422(2)	0.36002(8)	0.0206(6)	0.055(1)	0.0187(7)	0.0122(6)	0.0122(6)	0.0080(7)
O(6W)	4*e*	0.2164(1)	0.5517(2)	0.39437(8)	0.0259(7)	0.0486(9)	0.0199(7)	0.0118(6)	0.0163(6)	0.0088(6)
O(11)	4*e*	–0.02310(9)	0.5974(2)	0.30227(8)	0.0262(7)	0.058(1)	0.0230(7)	0.0046(6)	0.0160(6)	–0.0033(7)
O(12)	4*e*	0.09547(9)	0.6858(2)	0.41148(8)	0.0214(7)	0.060(1)	0.0326(8)	–0.0032(6)	0.0164(6)	–0.0110(7)
O(13)	4*e*	0.0868(1)	0.8765(2)	0.59008(9)	0.0348(8)	0.065(1)	0.0319(8)	–0.0230(8)	0.0184(7)	–0.0230(8)
O(14)	4*e*	–0.0254(1)	0.8415(3)	0.60689(9)	0.0393(9)	0.093(2)	0.0300(9)	–0.0211(9)	0.0224(8)	–0.0299(9)
O(15)	4*e*	–0.2484(1)	0.4884(2)	0.37783(9)	0.0265(7)	0.051(1)	0.0247(8)	–0.0168(6)	0.0167(6)	–0.0138(6)
O(21)	4*e*	0.3115(1)	0.3316(3)	0.19593(9)	0.0240(7)	0.094(2)	0.0341(9)	0.0006(8)	0.0164(7)	–0.0224(9)
O(22)	4*e*	0.4345(1)	0.3636(3)	0.30942(9)	0.0334(8)	0.079(1)	0.0264(8)	0.0026(8)	0.0205(7)	–0.0103(8)
O(23)	4*e*	0.30919(9)	0.1374(2)	0.00896(8)	0.0259(7)	0.058(1)	0.0248(7)	–0.0113(6)	0.0134(6)	–0.0155(7)
O(24)	4*e*	0.4252(1)	0.1592(3)	–0.00398(8)	0.0307(7)	0.076(1)	0.0241(8)	–0.0126(7)	0.0173(7)	–0.0182(8)
O(25)	4*e*	0.67793(9)	0.3592(2)	0.25279(8)	0.0211(7)	0.069(1)	0.0287(8)	–0.0119(7)	0.0147(6)	–0.0226(7)
N(1)	4*e*	–0.0047(1)	0.7234(2)	0.46334(9)	0.0188(7)	0.0310(9)	0.0208(8)	–0.0018(6)	0.0102(6)	–0.0043(6)
N(2)	4*e*	0.4084(1)	0.2546(2)	0.14385(9)	0.0199(7)	0.0316(9)	0.0199(8)	–0.0003(6)	0.0107(6)	–0.0060(6)
N(3)	4*e*	0.3169(2)	–0.1055(3)	0.5082(1)	0.093(2)	0.038(1)	0.030(1)	–0.016(1)	0.020(1)	0.0018(9)
C(1)	4*e*	0.2976(3)	–0.1482(6)	0.5618(2)	0.144(3)	0.087(2)	0.060(2)	–0.036(2)	0.053(2)	0.004(2)
C(2)	4*e*	0.4008(3)	–0.1726(5)	0.5187(2)	0.078(2)	0.058(2)	0.067(2)	0.016(2)	–0.002(2)	0.008(2)
C(3)	4*e*	0.2565(2)	–0.0217(3)	0.4481(2)	0.059(2)	0.032(1)	0.037(1)	–0.008(1)	0.021(1)	–0.004(1)
C(11)	4*e*	–0.0434(1)	0.6441(2)	0.3980(1)	0.0206(8)	0.028(1)	0.0184(9)	0.0027(7)	0.0120(7)	–0.0006(7)
C(12)	4*e*	–0.1264(1)	0.5652(3)	0.3661(1)	0.0205(8)	0.030(1)	0.0166(8)	–0.0010(7)	0.0088(7)	–0.0034(7)
C(13)	4*e*	–0.1705(1)	0.5681(3)	0.4030(1)	0.0184(8)	0.031(1)	0.0184(9)	–0.0028(7)	0.0092(7)	–0.0034(7)
C(14)	4*e*	–0.1283(1)	0.6563(3)	0.4704(1)	0.0243(8)	0.034(1)	0.0184(9)	–0.0028(7)	0.0129(8)	–0.0041(8)
C(15)	4*e*	–0.0451(1)	0.7326(3)	0.4994(1)	0.0237(8)	0.029(1)	0.0162(8)	0.0002(7)	0.0106(7)	–0.0044(7)
C(16)	4*e*	0.0147(1)	0.6433(3)	0.3672(1)	0.0225(8)	0.035(1)	0.0244(9)	0.0056(7)	0.0162(8)	0.0020(8)
C(17)	4*e*	0.0099(1)	0.8256(3)	0.5728(1)	0.0276(9)	0.036(1)	0.0197(9)	–0.0049(8)	0.0108(8)	–0.0098(8)
C(21)	4*e*	0.4530(1)	0.3121(2)	0.2134(1)	0.0221(8)	0.029(1)	0.0181(9)	0.0016(7)	0.0126(7)	–0.0036(7)
C(22)	4*e*	0.5437(1)	0.3498(3)	0.2512(1)	0.0233(8)	0.035(1)	0.0188(9)	–0.0014(7)	0.0120(8)	–0.0069(8)
C(23)	4*e*	0.5917(1)	0.3296(3)	0.2177(1)	0.0196(8)	0.034(1)	0.0224(9)	–0.0018(7)	0.0115(8)	–0.0079(8)
C(24)	4*e*	0.5402(1)	0.2762(3)	0.1434(1)	0.0248(9)	0.040(1)	0.0215(9)	–0.0024(8)	0.0156(8)	–0.0088(8)
C(25)	4*e*	0.4498(1)	0.2370(3)	0.1086(1)	0.0218(8)	0.028(1)	0.0186(9)	–0.0002(7)	0.0116(7)	–0.0043(7)
C(26)	4*e*	0.3950(1)	0.3372(3)	0.2434(1)	0.0260(9)	0.037(1)	0.026(1)	0.0010(8)	0.0188(8)	–0.0054(8)
C(27)	4*e*	0.3901(1)	0.1720(3)	0.0305(1)	0.0226(8)	0.032(1)	0.0195(9)	–0.0024(7)	0.0096(8)	–0.0072(8)

Acknowledgments. We gratefully acknowledge the financial support by the NSF of China (grant no. 20801026), and the NSF of Jiangxi Province (grant no. 2008GQC0036).

References

1. Gao, S.; Liu, J.-W.; Huo, L.-H.; Zhao, H.; Zhao, J.-G.: Hexaaquachromium(III) triaquabis(benzene-1,3-dioxyacetato)sodate(I) pentahydrate. Acta Crystallogr. **E60** (2004) m662-m664.
2. Eshel, M.; Bino, A.: Hexaaquachromium(III) tracetate. Inorg. Chim. Acta **320** (2001) 127.
3. Dalrymple, S. A.; Parvez, M.; Shimizu, G. K. H.: Intra- and Intermolecular Second-Sphere Coordination Chemistry: Formation of Capsules, Half-Capsules, and Extended Structures with Hexaaquo- and Hexaammine-metal Ions. Inorg. Chem. **41** (2002) 6986-6996.
4. Xing, Q.-J.; Chen, M.-H.; Xie, Y.; Dai, S.-C.; Zhang, L.-Z.; Zou, J.-P.: Crystal structure of tetraaqua(4-oxo-pyridine-2,6-dicarboxylato-*N*,*O*,*O'*)-lanthanum(III) monohydrate, $La(H_2O)_4(C_7H_2NO_5) \cdot H_2O$. Z. Kristallogr. NCS. **225** (2010) 671-672.
5. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.