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The crystal structure of dichlorido-(tris(2-benzimidazolylmethyl)amine- κ^4N,N',N'',N''')chromium(III) chloride – methanol (1/3), $\text{CrC}_{27}\text{H}_{33}\text{Cl}_3\text{N}_7\text{O}_3$

Table 1: Data collection and handling.

Crystal:	Block, green
Size:	0.15 × 0.12 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.69 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13443, 7221, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5873
$N(\text{param})_{\text{refined}}$:	391
Programs:	Bruker programs [1], SHELX [2–4], DIAMOND [5], OLEX2 [6]

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Abstract

$\text{CrC}_{27}\text{H}_{33}\text{Cl}_3\text{N}_7\text{O}_3$, triclinic, $P\bar{1}$ (no. 2), $a = 9.7862(13)$ Å, $b = 12.4690(17)$ Å, $c = 12.8413(17)$ Å, $\alpha = 84.163(2)^\circ$, $\beta = 73.602(3)^\circ$, $\gamma = 85.524(2)^\circ$, $V = 1493.4(3)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0472$, $wR_{\text{ref}}(F^2) = 0.1524$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Tris(2-benzimidazolylmethyl)amine (NTB) was prepared according to an earlier reported method [7]. NTB (0.408 g, 1.0 mmol) was dissolved in hot methanol (50.0 mL) and then a solution of CrCl_3 (0.158 g, 1.0 mmol) in 20.0 mL methanol was added drop by drop. The mixed solution was stirred for 30 min at 50 °C. Finally, the reaction mixture was filtered and the filtrate solution was evaporated at room temperature

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr1	0.87932(4)	0.24696(3)	0.35537(3)	0.01037(12)
O1	0.5572(2)	0.10643(17)	1.08021(17)	0.0294(5)
H1	0.597(4)	0.0454(16)	1.087(3)	0.044*
O2	0.9564(2)	0.19453(16)	0.86432(15)	0.0232(4)
H2	1.030(2)	0.157(2)	0.866(3)	0.035*
O3 ^a	0.4809(3)	0.1332(2)	0.7181(2)	0.0396(8)
H3A ^a	0.4251	0.1419	0.7799	0.059*
O3 ^b	0.5987(13)	0.1141(7)	0.6653(9)	0.0396(8)
H3 ^b	0.6877	0.1025	0.6473	0.059*
Cl1	0.82188(6)	0.39065(4)	0.45741(4)	0.01619(14)
Cl2	0.91378(6)	0.13139(5)	0.50164(4)	0.01610(14)
Cl3	0.23008(6)	0.09169(5)	0.92587(5)	0.01804(14)
N1	0.9336(2)	0.11276(15)	0.25366(15)	0.0117(4)
N2	0.8550(2)	0.32773(15)	0.21376(16)	0.0127(4)
N3	0.8637(2)	0.31986(16)	0.03942(16)	0.0151(4)
H3	0.895(3)	0.294(2)	−0.0247(13)	0.018*
N4	1.0931(2)	0.26305(15)	0.29001(16)	0.0123(4)
N5	1.3009(2)	0.19395(16)	0.19269(16)	0.0148(4)
H5A	1.367(2)	0.1476(19)	0.161(2)	0.018*
N6	0.6845(2)	0.18585(15)	0.38087(15)	0.0129(4)
N7	0.5594(2)	0.04882(16)	0.36851(16)	0.0145(4)
H7A	0.534(3)	−0.0141(13)	0.358(2)	0.017*
C1	0.9177(3)	0.14815(18)	0.14170(19)	0.0152(5)
H1A	1.0085	0.1323	0.0862	0.018*
H1B	0.8428	0.1072	0.1278	0.018*
C2	0.8787(2)	0.26562(19)	0.13211(18)	0.0127(4)
C3	0.8258(2)	0.43219(18)	0.17069(18)	0.0126(4)
C4	0.7961(3)	0.53062(19)	0.2178(2)	0.0159(5)
H4	0.7916	0.5353	0.2921	0.019*
C5	0.7736(3)	0.6211(2)	0.1513(2)	0.0195(5)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H5	0.7541	0.6893	0.1807	0.023*
C6	0.7787(3)	0.6146(2)	0.0420(2)	0.0207(5)
H6	0.7624	0.6786	−0.0007	0.025*
C7	0.8067(3)	0.5180(2)	−0.0053(2)	0.0199(5)
H7	0.8094	0.5135	−0.0793	0.024*
C8	0.8309(3)	0.4276(2)	0.0608(2)	0.0156(5)
C9	1.0847(2)	0.07642(19)	0.2481(2)	0.0148(5)
H9A	1.1276	0.0364	0.1829	0.018*
H9B	1.0890	0.0287	0.3137	0.018*
C10	1.1626(2)	0.17676(18)	0.24190(18)	0.0132(4)
C11	1.1930(2)	0.34181(19)	0.27076(19)	0.0133(4)
C12	1.1792(3)	0.44687(19)	0.30174(19)	0.0147(4)
H12	1.0905	0.4770	0.3428	0.018*
C13	1.3013(3)	0.5055(2)	0.2697(2)	0.0185(5)
H13	1.2961	0.5770	0.2904	0.022*
C14	1.4323(3)	0.4623(2)	0.2076(2)	0.0209(5)
H14	1.5126	0.5059	0.1859	0.025*
C15	1.4469(3)	0.3571(2)	0.1772(2)	0.0197(5)
H15	1.5357	0.3270	0.1364	0.024*
C16	1.3246(3)	0.29844(19)	0.20976(19)	0.0148(5)
C17	0.8306(2)	0.02783(18)	0.30757(19)	0.0142(4)
H17A	0.8242	−0.0223	0.2543	0.017*
H17B	0.8616	−0.0142	0.3674	0.017*
C18	0.6898(3)	0.08606(19)	0.35124(18)	0.0139(4)
C19	0.5399(2)	0.21641(19)	0.42022(18)	0.0127(4)
C20	0.4731(3)	0.3126(2)	0.46055(19)	0.0159(5)
H20	0.5263	0.3721	0.4639	0.019*
C21	0.3258(3)	0.3171(2)	0.4954(2)	0.0189(5)
H21	0.2767	0.3810	0.5243	0.023*
C22	0.2464(3)	0.2297(2)	0.48932(19)	0.0189(5)
H22	0.1453	0.2364	0.5138	0.023*
C23	0.3115(3)	0.1343(2)	0.44872(19)	0.0162(5)
H23	0.2579	0.0753	0.4449	0.019*
C24	0.4607(3)	0.12970(19)	0.41353(18)	0.0140(4)
C25	0.5900(3)	0.1465(3)	0.9689(2)	0.0290(6)
H25A	0.5302	0.2120	0.9611	0.043*
H25B	0.5717	0.0917	0.9256	0.043*
H25C	0.6907	0.1636	0.9431	0.043*
C26	0.9777(3)	0.2404(2)	0.7549(2)	0.0297(6)
H26A	0.9376	0.3149	0.7552	0.045*
H26B	0.9301	0.1980	0.7165	0.045*
H26C	1.0801	0.2398	0.7179	0.045*
C27	0.5644(3)	0.2223(2)	0.6994(2)	0.0305(6)
H27A ^a	0.5039	0.2877	0.6930	0.046*
H27B ^a	0.6411	0.2166	0.6317	0.046*
H27C ^a	0.6038	0.2246	0.7612	0.046*
H27D ^b	0.6496	0.2644	0.6723	0.046*
H27E ^b	0.4885	0.2563	0.6692	0.046*
H27F ^b	0.5335	0.2196	0.7791	0.046*

Occupancies: ^a0.800(4), ^b0.200(4).

for ten days. Some green block crystals were obtained at the bottom of the vessel (0.50 g, yield: 75%).

Experimental details

Hydrogen atoms bonded to carbon atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms with C–H = 0.95 Å (aromatic), 0.99 Å (methylene), 0.98 Å (methyl) $U_{iso}(H) = 1.2U_{eq}$ (aromatic and methylene) and $1.5U_{eq}$ (methyl). Hydrogen atoms bonded to nitrogen, O1 and O2 atoms were initially found from the difference maps and refined with the restraints of N–H = 0.88(1) Å, O–H = 0.84(1) Å. The positions of hydrogen atoms bonded to disordered O3 and O3' were constrained to be at the 'best' positions, forming hydrogen bonds to neighboring chloride anions [3]. Commands DFIX and SADI were used in the refinement to restrain C–O, N–H and O–H distances, and EADP was used to restrain the thermal factor of O3' being similar to O3. For the N and O atoms, $U_{iso}(H) = 1.2U_{eq}(N)$ and $1.5U_{eq}(O)$.

Comment

The multi-benzimidazole ligand tris(2-benzimidazolylmethyl) amine (NTB) has been often used in the design and synthesis of metal-containing compounds due to their potential application in the fields of biological and bioinorganic chemistry [8–10]. NTB has been often seen to be a tetradentate ligand coordinating a late transition metal. Compared to these metal complexes, early transition metal complexes of NTB are rarely reported.

The asymmetric unit of the title structure is composed of each one $[Cr(NTB)Cl_2]^+$, one Cl^- anion and three methanol solvent molecules. NTB acts as a tetradentate ligand, coordinating through the tertiary N atom and three benzimidazole (bzim) N atoms to metal ion. Two chlorido ligands are in a *cis* configuration. The N_4Cl_2 donor set constructs an octahedral polyhedron around the central Cr(III). The tertiary N1 atom presents a bond length about 0.10 Å longer than those for the three bzim N atoms. To retain the octahedral geometry, ligand NTB adopts a planar geometry with a dihedral angle of 11.9(1)° between the N4/N5 and N6/N7-containing bzim groups. However, the angles of these moieties with the third one are 79.9(1) and 88.3(1)°, respectively, which are very similar to its analogous structure with different solvent [11]. By considering some NTB-containing analogs as a whole, it can be found NTB can adopt many spatial arrangements to meet the coordination preference of a metal ion or solvent molecules [12–14]. On the other hand, the Cr(III) ion lies in the plane formed by N1, N4, N6 and CL1 atoms (maximal deviation: 0.025 Å for Cr1). As a result of these features, the deviations from an ideal octahedral geometry around Cr (III) ion are the following: *trans*

angles range from $158.09(8)$ to $178.29(5)^\circ$ and *cis* angles from $78.92(7)$ to $101.19(6)^\circ$.

A detailed geometrical analysis using the program PLATON [15] indicates that these adjacent $[\text{Cr}(\text{NTB})\text{Cl}_2]^+$ ions are firstly linked into two-dimensional layers parallel to the (011) plane by three $\pi \cdots \pi$ interactions. These layers are further linked by three $\text{N}-\text{H} \cdots \text{O}$ and three $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonds into the final three-dimensional network.

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