Crystal structure of bis(diethylenetriamine)cobalt(II) tetrahydroxypentaborate, $[Co(C_4H_{13}N_3)_2][B_5O_6(OH)_4]_2$

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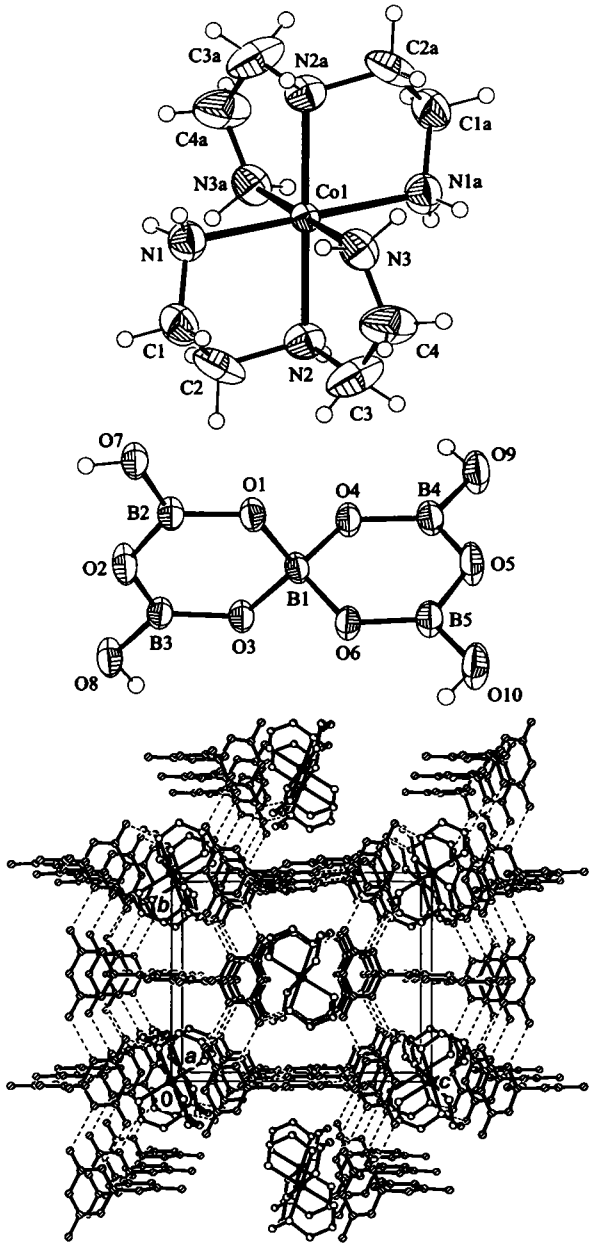

Abstract

$C_8H_{34}B_{10}CoN_6O_{20}$, monoclinic, $P12_1/c1$ (no. 14), $a = 8.551(2)$ Å, $b = 11.770(3)$ Å, $c = 14.508(3)$ Å, $\beta = 91.169(3)°$, $V = 1459.8$ Å^3, $Z = 2$, $R_{gt}(F) = 0.051$, $wR_{ref}(F^2) = 0.144$, $T = 298$ K.

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Source of material

The orange single crystals of title compound were prepared from a mixture of $CoSO_4 \cdot 7H_2O$ (1.4055 g), H_3BO_3 (1.3910 g), DETA (diethylenetriamine, 1.7 ml), pyridine (1 ml) and H_2O (10 ml) in the molar ratio of 1:4.5:3:5:15. The mixture was stirred until a homogeneous solution was obtained, further sealed in a 30 ml Teflon-lined stainless steel vessel and heated at 453 K for about 5 days.

Discussion

The synthesis of new organic-inorganic hybrid compounds is a relatively new research area that has developed rapidly in the last several years. Boron atoms are with oxygen not only in fourfold (tetrahedral, BO_4), but also in threefold coordination (triangular, BO_3). These BO_3 and BO_4 groups may further link together though common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks [1]. The formation of metallo-organically templated borate is less explored. Only few compounds such as $[Cu(en)_2][B_7O_{13}H_3]_n$ [2] and $[Mn(C_{10}H_{18}N_6)][B_5O_6(OH)_4]_2$ [3] have been reported.

The crystal structure of $[Co(C_4H_{13}N_3)_2][B_5O_6(OH)_4]_2$ consists of $[Co(C_4H_{13}N_3)_2]^{2+}$ cations and $[B_5O_6(OH)_4]^-$ polyborate anions. The Co atom is bonded to the six N atoms from two ligands of diethylenetriamine molecules forming an octahedron (figure, top). The Co—N distances range from 2.145(3) Å to 2.196(3) Å and the N–Co–N angles are between 79.3(1)° and 180.0 (2)°. The isolated pentaborate anion is characterized by two $[B_3O_3]$ rings linked by a boron atom forming a common BO_4 tetrahedron. Each ring is formed by two BO_3 triangles and a slightly distorted common BO_4 tetrahedron (figure, middle). The terminal oxygen atoms are protonated. The B—O distances for the trigonal B atoms (B2, B4, B3 and B5) range from 1.344(5) Å to 1.391(5) Å and the O–B–O angles are in the range 115.6(3)° – 123.7(3)°. The B—O distances for the tetrahedral B1 atom range from 1.458(4) Å to 1.473(4) Å and the O–B–O angles are in the range 108.2(3)° – 119.2(3)°. The $[B_5O_6(OH)_4]^-$ anions form a three-dimensional structure through hydrogen bonds with channels along the *a* and *c* axes. Especially, there are large channels containing 12-membered boron rings along the *a* axis, between which $[Co(C_4H_{13}N_3)_2]^{2+}$ cations are intercalated. In the compound, four short O···O distances are found which can be explained in terms of O–H···O hydrogen bonds, with O···O distances between 2.696 Å and 2.845 Å. The $[Co(C_4H_{13}N_3)_2]^{2+}$ cations are located in the inorganic channel and interact with the framework both electrostatically and though hydrogen bonds, with N···O distances in the range 2.943 Å – 3.419 Å (figure, bottom).

Table 1. Data collection and handling.

Crystal:	orange prism, size 0.19 x 0.45 x 0.53 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.79 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7172, 2513
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1897
$N(param)_{refined}$:	205
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.2930	0.0678	–0.0145	0.072
H(1B)	4e	0.2388	0.0407	–0.1079	0.072
H(2)	4e	–0.1853	0.1477	–0.0762	0.065
H(3A)	4e	–0.0008	0.0531	0.1744	0.069
H(3B)	4e	0.1218	0.1217	0.1333	0.069
H(7)	4e	–0.1126	1.0175	0.6424	0.066
H(8)	4e	0.3919	1.0053	0.4357	0.067
H(9)	4e	0.5866	0.7633	0.8225	0.085
H(10)	4e	0.5884	1.2668	0.8168	0.092
H(1C)	4e	0.1967	0.2400	–0.0163	0.090
H(1D)	4e	0.2582	0.2257	–0.1170	0.090
H(2A)	4e	0.0154	0.1726	–0.1690	0.096
H(2B)	4e	0.0025	0.2904	–0.1190	0.096
H(3C)	4e	–0.0733	0.3055	0.0251	0.110
H(3D)	4e	–0.2376	0.2488	0.0347	0.110
H(4A)	4e	–0.1747	0.1689	0.1521	0.118
H(4B)	4e	–0.0326	0.2519	0.1552	0.118

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}
Co(1)	2a	0	0	0	0.0326(4)	0.0367(4)	0.0261(4)	–0.0010(2)	–0.0034(2)	0.0017(2)
B(1)	4e	0.3786(4)	1.0131(3)	0.7008(2)	0.028(2)	0.038(2)	0.025(2)	0.003(1)	–0.006(1)	0.003(1)
B(2)	4e	0.0967(4)	1.0178(3)	0.6601(2)	0.029(2)	0.043(2)	0.028(2)	0.003(1)	–0.004(1)	–0.002(2)
B(3)	4e	0.2787(4)	1.0131(3)	0.5389(2)	0.026(2)	0.043(2)	0.029(2)	0.000(1)	–0.004(1)	–0.001(2)
B(4)	4e	0.5585(4)	0.9139(3)	0.8116(3)	0.040(2)	0.040(2)	0.035(2)	0.001(2)	–0.012(2)	0.002(2)
B(5)	4e	0.5597(5)	1.1163(3)	0.8079(3)	0.039(2)	0.040(2)	0.040(2)	0.002(2)	–0.014(2)	–0.001(2)
N(1)	4e	0.2131(4)	0.0759(3)	–0.0553(2)	0.057(2)	0.061(2)	0.063(2)	–0.005(2)	0.007(2)	–0.002(2)
N(2)	4e	–0.0942(4)	0.1603(3)	–0.0443(2)	0.056(2)	0.059(2)	0.046(2)	0.006(2)	–0.011(2)	0.001(2)
N(3)	4e	0.0227(4)	0.0970(3)	0.1258(2)	0.069(2)	0.064(2)	0.040(2)	–0.008(2)	–0.003(2)	0.001(2)
O(1)	4e	0.2136(3)	1.0149(2)	0.7242(2)	0.030(1)	0.055(2)	0.024(1)	0.001(1)	–0.0031(9)	–0.0004(9)
O(2)	4e	0.1277(3)	1.0206(2)	0.5678(2)	0.027(1)	0.094(2)	0.025(1)	0.005(1)	–0.0039(9)	0.001(1)
O(3)	4e	0.3993(2)	1.0099(2)	0.6004(2)	0.026(1)	0.045(1)	0.026(1)	0.0015(9)	–0.0035(9)	0.0001(9)
O(4)	4e	0.4522(2)	0.9112(2)	0.7410(2)	0.036(1)	0.036(1)	0.036(1)	–0.0001(9)	–0.0138(9)	0.0011(9)
O(5)	4e	0.6070(3)	1.0149(2)	0.8490(2)	0.061(2)	0.042(2)	0.051(2)	0.002(1)	–0.036(1)	–0.001(1)
O(6)	4e	0.4555(2)	1.1164(2)	0.7369(1)	0.035(1)	0.035(1)	0.034(1)	–0.0005(9)	–0.0124(9)	–0.0019(9)
O(7)	4e	–0.0537(3)	1.0158(2)	0.6877(2)	0.029(1)	0.074(2)	0.029(1)	0.000(1)	–0.0017(9)	0.001(1)
O(8)	4e	0.2983(3)	1.0092(2)	0.4466(2)	0.026(1)	0.085(2)	0.024(1)	0.003(1)	–0.0021(9)	–0.001(1)
O(9)	4e	0.6225(3)	0.8195(2)	0.8488(2)	0.064(2)	0.041(1)	0.062(2)	–0.000(1)	–0.038(1)	0.006(1)
O(10)	4e	0.6227(3)	1.2111(2)	0.8446(2)	0.073(2)	0.040(2)	0.070(2)	–0.003(1)	–0.046(2)	–0.003(1)
C(1)	4e	0.1840(6)	0.1971(4)	–0.0730(4)	0.079(3)	0.054(3)	0.093(4)	–0.016(2)	0.025(3)	0.005(2)
C(2)	4e	0.0246(7)	0.2104(4)	–0.1097(3)	0.130(5)	0.047(3)	0.064(3)	–0.008(3)	–0.006(3)	0.022(2)
C(3)	4e	–0.1261(7)	0.2336(5)	0.0341(4)	0.102(4)	0.089(4)	0.083(3)	0.050(3)	–0.020(3)	–0.027(3)
C(4)	4e	–0.0803(9)	0.1901(5)	0.1204(3)	0.180(6)	0.061(3)	0.055(3)	0.034(3)	0.007(3)	–0.012(2)

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