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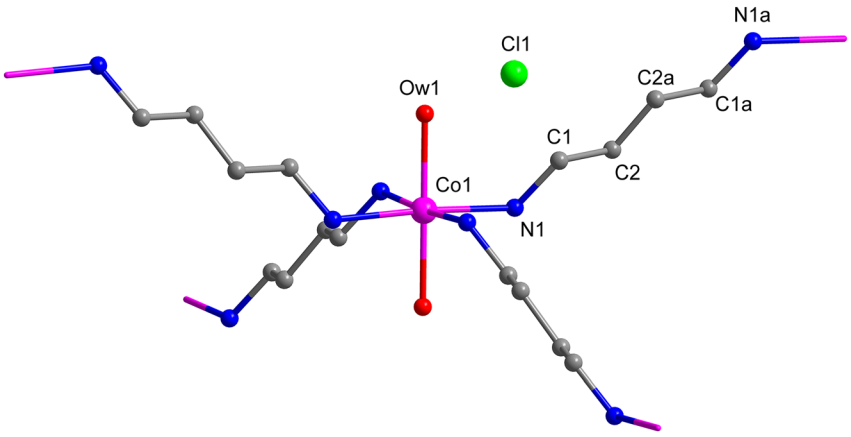
Crystal structure of poly[diaqua-bis(μ_2-1,4-diaminobutane-*N*:*N*′)cobalt(II)] dichloride, $C_8H_{28}Cl_2CoN_4O_2$



https://doi.org/10.1515/ncrs-2022-0227
Received May 2, 2022; accepted May 19, 2022;
published online February 24, 2023

Abstract

$C_8H_{28}Cl_2CoN_4O_2$, orthorhombic, *Fddd* (no. 70), a = 10.116(2) Å, b = 13.532(3) Å, c = 23.507(5) Å, V = 3217.8(11) Å^3, Z = 8, $R_{gt}(F)$ = 0.0361, $wR_{ref}(F^2)$ = 0.1069, T = 100.5 K.

CCDC no.: 2173635

A part of the title coordination polymer 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.

Table 1: Data collection and handling.

Crystal:	Orange poly
Size:	0.09 × 0.07 × 0.07 mm
Wavelength:	Synchrotron radiation (0.60997 Å)
μ:	0.91 mm^{-1}
Diffractometer, scan mode:	Rayonix MX225HS, ω
θ_{max}, completeness:	29.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11425, 1837, 0.103
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 1637
$N(param)_{refined}$:	44
Programs:	BL2D-SMC [1], Data processing [2], SHELX [3, 4], Diamond [5], Data collection [6]

Source of material

The mixture of $CoCl_2{\cdot}6H_2O$ (0.071 g, 0.3 mmol), 1,4-diaminobutane (0.090 mL, 0.9 mmol), muconic acid (0.043 g, 0.3 mmol) in ethanol (1.0 mL) was sealed under a vacuum in a Pyrex tube and heated to 70 °C for 68 h, then cooled to room temperature at 20 °C/h. The pH before and after the reaction were 8 and 7, respectively. The orange polyhedral crystals were recovered with unidentified light blue, violet, and white powder after vacuum filtration. The product is stable in air.

Experimental details

The data collection was carried out using synchrotron X-ray radiation on a Rayonix MX225HS CCD detector with a silicon(111) double-crystal monochromator at BL2D–SMC beamline of the Pohang Accelerator Laboratory, Korea. The PAL BL2D–SMDC program [1] was used for data collection, and HKL3000sm [2] was used for cell refinement, data

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.375000	0.375000	0.375000	0.00666 (9)
Cl1	0.625000	0.625000	0.43061 (2)	0.01384 (10)
O1W	0.375000	0.53230 (10)	0.375000	0.0159 (2)
H1	0.3206 (19)	0.5638 (15)	0.3642 (8)	0.024*
N1	0.52885 (8)	0.38060 (6)	0.44036 (4)	0.01040 (16)
H00E	0.573027	0.436918	0.435769	0.012*
H00F	0.488761	0.383971	0.474006	0.012*
C1	0.62708 (10)	0.29972 (10)	0.44334 (5)	0.0188 (2)
H00C	0.690223	0.308325	0.412686	0.023*
H00D	0.581855	0.237471	0.437046	0.023*
C2	0.70204 (10)	0.29329 (9)	0.49889 (4)	0.0175 (2)
H00A	0.639232	0.287023	0.529862	0.021*
H00B	0.750863	0.354196	0.504545	0.021*

integration, and absorption correction. The structure was solved using Direct Methods and refined by SHELXT and ShelxLe with the SHELXL plug-in [3, 4]. All hydrogen atoms bound to carbon and nitrogen atoms were placed in calculated positions and refined as riding model, and their positions and isotropic displacement parameters were refined.

Comment

The aliphatic diamine with two donor sites, 1,4-diaminobutane (dab) acts as a chelating agent in some cases, but it was mainly observed to act as a bridging ligand. The simple case where dab is used as a bridging ligand are the chain structures found in Cd(dab)X_2 (X=Cl, Br), Hg(dab)Cl$_2$ [7], and [Cd{SSi(O*t*Bu)$_3$}$_2$(dab)(CH$_3$OH)]$_n$ [8] in which the metal cation is coordinated by two bridging dab and two terminal ligands. Although very rare, there is an example that a metal cation is linked by four bridging dab to show an extending 2D polymeric structure, [Cu(dab)$_2$(ClO$_4$)$_2$]$_n$(H$_2$O)$_{2n}$ [9]. In [Cu(dab)$_2$(ClO$_4$)$_2$]$_n$(H$_2$O)$_{2n}$, Cu(II) is equatorially coordinated by four N atoms from four dab. Two weakly bonded water molecules to Cu in *trans*–configuration complete an elongated octahedral geometry. Each of Cu(II) is in turn linked through dab, which extends to a 2D network with square-shaped voids.

Herein, we report a novel cobalt complex, Co(1,4–diaminobutane)$_2$(H$_2$O)·2Cl. To the best of our knowledge, this is the first 3D framework structure linked by the dab ligand. The crystal structure of the title compound is built of a 3D network with a diamonoid topology [10]. One crystallographically unique cobalt atom is coordinated with four nitrogen atoms from four symmetry related dab ligands (d(Co—N) = 2.1881(8) Å). The water molecules in *trans*–configuration (d(Co—O) = 2.2182(14) Å) complete the slightly distorted octahedral environment of Co1. The bond valence sum (BVS) calculation for Co gives a value of +2.18, indicating an oxidation state of +2 [11]. Each CoN_4O_2 octahedron is linked by four neighboring octahedra through dab ligands in a distorted tetrahedral geometry with the Co—Co—Co angles of 83.578(1)°, 109.446(1)° and 141.164(1)°, which extend to a diamond-type topological network, $[Co(dab)_2(H_2O)_2]^{2+}$. The framework contains distorted hexagonal-shaped 6-membered ring including the CoN_4O_2 octahedra. The $\{Co\}_6$ rings intersect each other, forming crossing channels in the [011] direction. The hexagonal rings have wide and narrow regions; the shortest opposite C···C distance is 12.52 Å, and the longest is 15.3 Å. The chloride ions balance the framework charge and are located in the channels.

Acknowledgments: J. Do thank the Pohang Accelerator Laboratory for beamline use (2022-2nd-2D-030).
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This research was supported by the (NRF) grant funded by the Korea government (MSIT) (No. 2021R1F1A1060277).
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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