SYNTHESIS, STRUCTURE AND INVESTIGATION OF GERMANIUM(IV) AND COPPER(II) COMPLEXES WITH MALIC ACID AND 1,10'-PHENANTHROLINE

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Abstract. Two crystalline compounds of germanium(IV) with malic acid (H_3Mal) and 1,10'-phenanthroline (phen) - $[Ge(HMal)_2(phen)]\cdot phen\cdot 2H_2O$ (**1**) and $[CuCl(phen)_2][Ge(OH)(HMal)_2]$ (**2**) were synthesized for the first time and characterized by elemental analysis, IR spectroscopy and thermogravimetric analysis. Using single crystal X-ray diffraction, two different forms of germanium were elucidated: Ge^{4+} (**1**) and hydrolyzed $GeOH^{3+}$ (**2**) with a distorted octahedron and pyramid surrounding geometry, respectively.

Introduction

In the course of our systematical research towards complex formation of germanium(IV) with hydroxycarboxylic acids, which are different by the number and mutual position of hydroxyl and carboxyl groups, our group have previously synthesized and structurally characterized different ligand and heteronuclear coordination compounds with citric [1,2], tartaric [3,4] and xylaric acids [5,6]. Unexpectedly, it was not possible to obtain germanium(IV) complex with the monohydroxydicarboxylic malic acid under the same conditions. At the same time, such research is of great interest because of the properties of malic acid that plays the key role in plants and animals metabolism, and is involved in many biochemical processes, *e.g.*, the Krebs cycle [7]. It is also a versatile polydentate ligand, a large number of mono-, di- and polymeric coordination compounds of different metals with H_3Mal have been already structurally characterized [8-11].

In the past few years, there were synthesized a number of complex compounds containing the divalent tris(oxalato-O,O')germanate anion $[Ge(C_2O_4)_3]^{2-}$, or the neutral bis(oxalate-O,O')germanium fragment $[Ge(C_2O_4)_2]$, with cationic transition metal complexes of 1,10-phenanthroline (phen):

$[M(phen)_3][Ge(C_2O_4)_3]xH_2O$ (where $M^{2+}=Cu^{2+}$, Fe^{2+}, Ni^{2+}, Co^{2+}), $[MGe(phen)_2(\mu_2\text{-}OH)_2(C_2O_4)_2]$ (where $M^{2+}=Cd^{2+}$ and Cu^{2+}) [12,13]. Also, there were reported different ligand complexes with 1,10'-phenanthroline and malic acid that link metals to the supramolecular chain: $[Zn(HMal)(phen)(H_2O)]$, $[Co(HMal)(phen)(H_2O)]$, $[Fe(HMal)(phen)(H_2O)]$ [14]. As a result, the idea for obtaining the complexes of germanium(IV) with malic acid by reactions in GeO_2 – H_3Mal – phen – water and GeO_2 – H_3Mal – $CuCl_2$ – phen – water systems has appeared. Here, the synthesis, structural characterization and properties of the new complexes in the solid state and also their comparison with the previously obtained coordination compounds of germanium(IV) with hydroxycarboxylic acids is reported.

Experimental

The starting reagents for the complexes synthesis were germanium(IV) oxide (GeO_2, 99.99%), DL-malic acid (H_3Mal, 99%), 1,10'-phenanthroline (phen, 99%), copper(II) chloride dihydrate ($CuCl_2\cdot 2H_2O$, 99.99%) (all ©Sigma Aldrich).

Instrumentation

Elemental analysis for germanium and copper was performed using inductively coupled

plasma atomic emission spectroscopy (PerkinElmer Optima 2000 DV instrument), chlorine was quantified by mercurometry. The C, H, and N analysis was performed using Elemental Analyzer CE-440.

Thermogravimetric analysis (TGA) was carried out using a Q-1500D device at a heating rate of 10 °C/min, in air, in 20-1000 °C temperature range.

The IR spectra in the 4000-400 cm^{-1} range were recorded as potassium bromide pellets on a PerkinElmer Frontier spectrometer (The absorption bands were attributed according to the reference data for the starting malic acid and our earlier obtained germanium(IV) coordination compounds with hydroxycarboxylic acids [1–6] (*s. – strong, m. – middle, w. – weak*).

Crystal data for structures **1** and **2** were measured on an Xcalibur-3 diffractometer (graphite monochromated Mo-Kα radiation, CCD detector, φ and ω-scanning). The structures were solved by the direct method using SHELXTL package [15]. Full-matrix least-squares refinement against F^2 in anisotropic approximation was used for non-hydrogen atoms. Positions of hydrogen atoms were located from the electron density difference maps and refined by "riding" model with $Uiso = nUeq$ of the carrier atom ($n = 1.5$ for hydroxyl groups and $n = 1.2$ for other hydrogen atoms). CCDC 1513407-1513408 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained, free of charge, *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Full use of the CCDC package was also made for searching in the CSD Database [16].

Synthesis
[Ge(HMal)$_2$(phen)]·phen·2H$_2$O (1)

Germanium(IV) oxide (26.2 mg, 0.125 mmol), malic acid (33.5 mg, 0.25 mmol) and 1,10'-phenanthroline (45.0 mg, 0.25 mmol) were added to 100 mL of boiling water. Obtained solution was slowly evaporated to 5 mL (80°C) to give after 24 h the result of self-assembly reaction - the solid, from which single crystals suitable for X-ray crystallography were isolated.

Elemental composition, based on single-crystal data for C$_{32}$GeH$_{28}$N$_4$O$_{12}$ (M= 733.17 g/mol), analytically calculated in %: C 52.37, Ge 9.90, N 7.64, H 3.81; found for the as-synthesized bulk material (in %): C 52.24, Ge 10.05, N 7.18, H 3.72.

TGA data of **1** (weight losses, Δm): 80-230°C, endothermic peak 150°C (-5.0%); 270-360°C, endothermic peak 310°C (-36.7%); 520-690°C, exothermic peak 610°C (-44.0%).

Selected IR data for **1** (in cm^{-1}): ν(O-H)=3371m; ν(C-H ring)=3069w, 2925w; ν(C=O)=1722s; ν_{as}(COO$^-$)=1686s; ν(C-C, ring)=1588m, 1526m, 1496w; ν_s(COO$^-$)=1419m; ν(C-N)=1343m; ν(C-O)=1108s, 1057w; δ(C-H)=1041m, 987w, 947w, 905w; ν(Ge-N)=658m; ν(Ge-O)=717s.

Crystal data for **1** (*M*=733.17 g/mol): monoclinic, space group C2, *a*=17.714(7) Å, *b*=12.830(7) Å, *c*=7.273(3) Å, β=102.192(5), *V*=1615.6(1) Å^3, *Z*=2, *T*=294 K, μ(MoKα)=1.019 mm^{-1}, D_{calc}=1.507 g/cm^3, 5619 reflections measured, 2898 unique (R_{int} =0.036, R_{sigma} =0.052) which were used in all calculations. The final R_1 was 0.045 (I > 2σ(I)) and wR_2 was 0.122 (all data).

[CuCl(phen)$_2$][Ge(OH)(HMal)$_2$] (2)

In the first step, GeO$_2$ (104.6 mg, 1 mmol) and malic acid (268.2 mg, 2 mmol) were dissolved in 100 mL of hot water to make first working solution, which was then concentrated to 25 mL (50°C). In the second step, weighted portions of 1,10'-phenanthroline (360 mg, 2 mmol) and CuCl$_2$·2H$_2$O (170.5 mg, 1 mmol) were added to 25 mL of ethanol and then heated at 40 °C until the reagents were completely dissolved. In the third step, two working solutions cooled to the room temperature were mixed to allow obtaining the mild after 2 days, from which blue crystals were collected mechanically and analyzed by X-ray crystallography.

Elemental composition, based on single-crystal data for C$_{32}$ClCuGeH$_{25}$N$_4$O$_{11}$ (M=813.14) analytically calculated in %: C 47.23, Cl 4.36, Cu 7.80, Ge 8.93, H 3.07, N 6.88; found for the as-synthesized bulk material (in %): C 47.95, Cl 4.10, Cu 8.05, Ge 8.47, H 3.14, N 7.12.

TGA data of **2** (weight losses, Δm): 150-220°C, endothermic peak 170°C (-2.5%); 260-340°C, endothermic peak 300°C (-44.1%); 400-570°C, exothermic peak 550°C (-10.0%); 600-880°C, exothermic peak 710°C (-20.8%).

Selected IR data for **2** (in cm^{-1}): ν(C-H, aromatic)=2919w; ν(C=O)=1706m; ν_{as}(COO$^-$)=1650s; ν(C-C, ring)=1587w, 1519m; ν_s(COO$^-$)=1428m; ν(C-N)=1341m; ν(C-O)=1170m, 1106w; δ(C-H)=961w, 907w; δ(Ge-O-H)=853m; ν(Ge-O)=668m.

Crystal data for **2** (*M*=813.14 g/mol): monoclinic, space group P2$_1$, *a*=12.413(3) Å, *b*=9.823(3) Å, *c*=26.538(4) Å, β=103.105(6),

V=3151.5(3) Å^3, Z=4, T=294 K, μ(MoKα)=1.784 mm^{-1}, D_{calc}=1.714 g/cm^3, 26405 reflections measured, 10652 unique (R_{int}=0.080, R_{sigma}=0.099), which were used in all calculations. The final R_1 was 0.060 (I > 2σ(I)) and wR_2 was 0.130 (all data).

Results and discussion

Complexes **1** and **2** are crystalline solids with the molar ratio Ge : malate : phen = 1:2:2 (**1**) and Ge : malate : Cu : phen = 1:2:1:2 (**2**) that are stable in air.

The thermal decomposition of **1** starts with an endotherm peak in the temperature range 80-230 °C, which is coming along the elimination to the gas phase of two molecules of crystal water (calc. Δm=4.92%). While heating, further in a temperature range from 270 to 360 °C, complex **1** eliminates one molecule of phenanthroline and two CO_2 molecules from the malate ligands (calc. Δm=36.56%).

According to the calculated weight loss of the thermogravimetric curve of complex **2**, the first endotherm peak is accompanied by elimination of one water molecule to the gas phase (calc. Δm=2.2%). That molecule is formed by an interaction of the carboxyl proton with the inner sphere OH group bound to germanium [3]. The second endotherm peak from the thermogravimetric curve of **2** corresponds to the loss of two phenanthroline molecules (calc. Δm=44.3%).

Finally, complexes **1** and **2** undergo oxidative thermal degradation and combustion of the organic part of their molecules, with the corresponding one (for **1**) and two exothermic peaks (for **2**).

The presence in IR spectra of **1** and **2** ν(C=O), ν_{as}(COO$^-$) and ν_s(COO) absorption bands, which are typical for COOH and COO$^-$ groups, shows the presence of nonequivalent carboxyl groups (free and bound) in the complexes. The conclusion about how these groups are bonded with germanium is also made on the basis of the band corresponding to the Ge–O stretching vibrations, which is emergence in the IR spectra of complexes. The presence of the band responsible for the Ge–O–H bending vibrations implies the presence of the hydrolyzed form of germanium in the complex **2**.

The absorption band at ~1340 cm^{-1} can be assigned to the ν(CN) heterocycle, the bands at 1588, 1526, 1496 cm^{-1} (for **1**) and 1587, 1519 (for **2**) - to the ν(C-C) phenanthroline ring vibrations. The deformation vibrations δ(C-H) of the aromatic rings: planar vibrations at 1041 cm^{-1};

non-planar vibrations at 987-905 cm^{-1} region were found [17,18].

In the structures of complexes **1** and **2** two different forms of germanium are implemented: Ge^{4+} (**1**) and hydrolyzed GeOH^{3+} (**2**), wherein neutral complex and anion are formed, respectively. In **1** coordination number is 6, in **2** – 5, where germanium atom is coordinated with two malate anions HMal^{2-} in both cases and binds with 1,10'-phenanthroline in **1** and with hydroxyl group in **2**.

The compound **1** exists as a monohydrate of co-crystal with 1,10'-phenanthroline in 1:1 ratio (Figure 1). Molecules of complex and uncoordinated 1,10'-phenanthroline are in particular position on the axis of second-order symmetry.
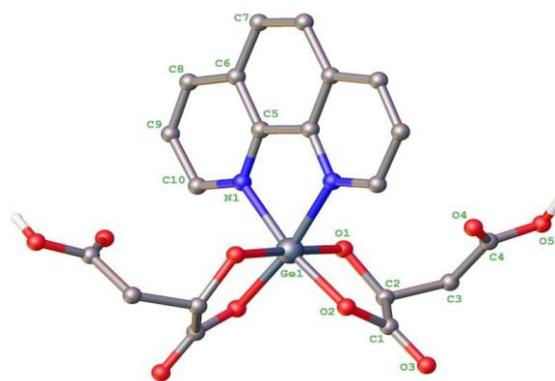
Figure 1. Molecular structure of 1.

The coordination polyhedron of Ge is a distorted octahedron. The Ge-O bond lengths are 1.818(3) Å and 1.912(5) Å, the Ge-N bond length is 2.057(3) Å. The O-Ge-O, O-Ge-N, N-Ge-N valence angles vary within 79.8(4)° ÷ 94.9(2)° (Table1).

In crystal structure of the molecules of coordination compound **1** and water are connected with intermolecular hydrogen bonds (Table 2) and form the three-dimensional network (Figure 2).

Table 1

Bond length (Å) and bond angles (°) in structures 1 and 2 (^{1}-x, 1-y, -z).

	Structure 1
Ge1-O1	1.818(3)
Ge1-O2	1.911(5)
Ge1-N1	2.057(6)
O1^1-Ge1-O2	91.6(2)
O1-Ge1-O2	87.1(2)
O1-Ge1-N1^1	94.9(2)
O1-Ge1-N1	86.5(2)
O2-Ge1-O2^1	93.6(3)
O2-Ge1-N1^1	93.7(9)
^{1}1-x,+y, 1-z	

Continuation of Table 1

Structure 2		
	Molecule A	**Molecule B**
Cu1-Cl1	2.315(3)	2.315(3)
Cu1-N1	2.103(7)	1.986(8)
Cu1-N2	1.994(8)	2.103(8)
Cu1-N3	2.107(8)	1.990(9)
Cu1-N4	1.987(8)	2.105(7)
Ge1-O1	1.793(7)	1.781(6)
Ge1-O2	1.910(6)	1.900(6)
Ge1-O6	1.773(7)	1.779(6)
Ge1-O7	1.936(6)	1.937(6)
Ge1-O11	1.741(7)	1.744(7)
N1-Cu1-Cl1	125.4(2)	123.6(2)
N1-Cu1-N3	112.5(3)	114.5(3)
N2-Cu1-Cl1	95.2(3)	91.8(3)
N2-Cu1-N1	80.6(3)	80.9(3)
N2-Cu1-N3	94.1(3)	97.9(3)
N3-Cu1-Cl1	122.0(2)	121.8(2)
N4-Cu1-Cl1	92.1(2)	92.8(3)
N4-Cu1-N1	96.1(3)	95.0(3)
N4-Cu1-N3	81.0(3)	81.1(3)
O1-Ge1-O2	87.7(3)	87.7(3)
O1-Ge1-O7	88.0(3)	86.7(3)
O6-Ge1-O1	124.4(3)	124.8(3)
O6-Ge1-O2	88.9(3)	90.8(3)
O6-Ge1-O7	86.9(3)	86.9(3)
O11-Ge1-O1	117.9(3)	119.5(3)
O11-Ge1-O2	98.1(3)	98.2(3)
O11-Ge1-O6	117.5(3)	115.3(3)
O11-Ge1-O7	91.0(3)	90.4(3)

Table 2

Geometric parameters of the hydrogen bonds in structures 1 and 2.

D-H...A	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
Structure I			
O5-H5…O6	1.77	2.586(8)	170.2
O6-H6B…O3[1]	2.01	2.839(10)	165.3
Structure II			
O5A-H5A…O8A[2]	1.98	2.695(11)	144.7
O10A-H10D…O4A	1.96	2.743(15)	160.1
O11A-H11D…O3A[3]	1.98	2.783(10)	142.6
O5B-H5B…O8B[4]	1.87	2.667(10)	163.6
O10B-H10C…O4B	2.18	2.974(15)	162.4
O11B-H11C…O3B[5]	2.24	2.840(10)	141.6

[1] 1/2-x, 1/2+y, 1-z [2] 1-x,-1/2+y, 1-z; [3] -x, 1/2+y, 1-z; [4] 1-x, 1/2+y, 2-z; [5] -x,-1/2+y, 2-z

Uncoordinated molecules of 1,10'-phenanthroline occupy cavities between neighborhood complexes. The distance between the π-systems of uncoordinated and coordinated phenanthroline molecules (3.38 Å) allows presuming the stacking interactions existence.

The negative charge of complex anion $[GeOH(HMal)_2]^-$ (Figure 3) in structure **2** is compensated by the complex cation $[CuCl(phen)_2]^+$ (Figure 4). In the independent part of unit cell, cations and anions of two types were found: A and B with several geometrical parameters difference.
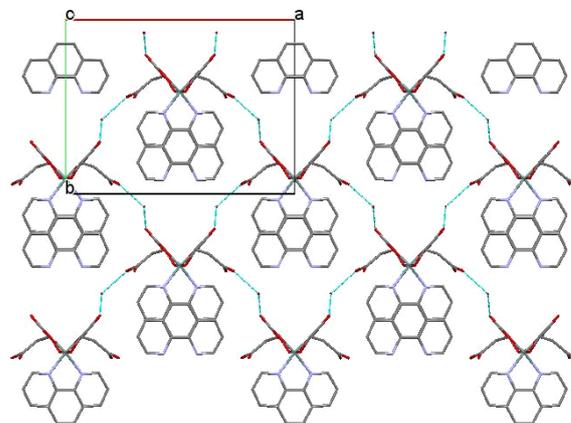
Figure 2. Molecules package in 1.

The coordination polyhedron of germanium atom in anion is a pyramid with distorted square in the base. The base of the pyramid is formed by oxygen atoms of deprotonated hydroxyl and carboxyl groups of malic acid (pseudo-torsion angle O(1)…O(2)…O(6)…O(7) shows the distortion rate of the base equals to 30º in anions A and B). There is the hydroxyl anion at the top of the pyramid. The negative charge of germanium coordination sphere leads to the changes in bond lengths of Ge-O (they vary within 1.741(7)÷1.935(7) Å in anion A and 1.744(7)÷1.937(6) Å in anion B (Table 1)). Valence angles of O-Ge-O bond have values within 86.9(3)÷117.9(3)º in anions A and B (ideal value is 90°). The position of the vacant carboxyl groups in anion is stabilized with an intermolecular hydrogen bond O(10)-H…O(4) (H…O 1.96 Å O-H…O 160º in anion A and H…O 2.18 Å O-H…O 162º in anion B).

The coordination polyhedron of Cu atom in complex cation of **2** represents the distorted trigonal bipyramid (Figure 4).

The N(1), N(3), Cl(1) atoms in cation A or N(2), N(4), Cl(1) in cation B are located in the equatorial planes, the N(2) and N(4) atoms in A or N(1) and N(3) in B, respectively, are located in the axial positions. The Cu-N bond lengths change within 1.988(8)÷2.106(9) Å in A and 1.987(8)÷2.104(8) Å in B, at the same time Cu-Cl length is equal to 2.315(3) Å in cation A and 2.314(3) Å in cation B (Table 1).
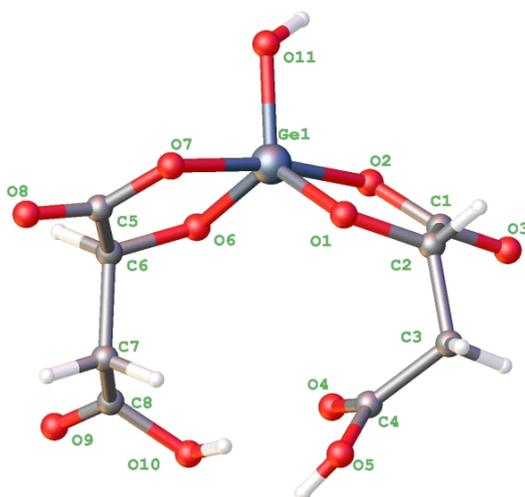
Figure 3. Molecular structure of anion [GeOH(HMal)₂]⁻ in 2.
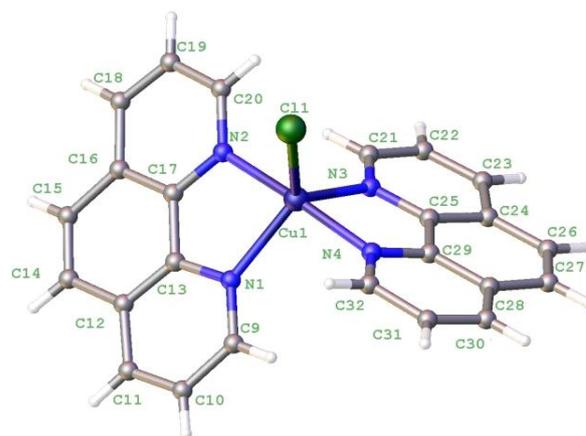
Figure 4. Molecular structure of cation [CuCl(phen)₂]⁺ in 2.
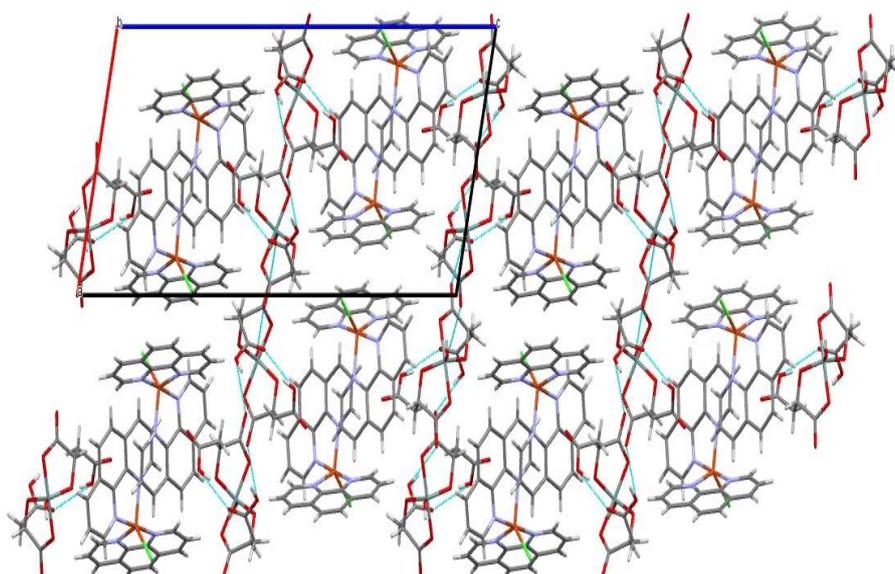
Figure 5. Crystal packing of compound 2 (projections along the *b* crystallographic axis).

The valence angles in cation A vary within $112.6(3) \div 125.4(2)°$ in the equatorial direction (the ideal value is 120°) and within $80.6(3) \div 96.1(3)°$ in the axial direction (the ideal value is 90°), in cation B $114.5(3) \div 123.7(2)°$ in the equatorial direction and within $80.9(3) \div 97.9(3)°$ in the axial direction.

In the crystal structure of **2** anions and cations form three types of alternating layers, parallel along the *ab* crystallographic plane (Figure 5): the first layer type is formed by anions A, the second layer type includes both cations (A and B) and the third layer type is organized by anions B. All anions within the layers are connected by the O-H…O intermolecular hydrogen bonds (Table 2).

Conclusions

Using 1,10'-phenanthroline, for the first time it was possible to get two different types of malatogermanate complexes of germanium: the different-ligand compound **1** by the self-assembly method from the water solution and the different-metal compound **2** by stepwise synthesis method from the water-ethylene solution. The feature of compound **1** is that 1,10'-phenanthroline enters the inner sphere and coordinates in a bidentate fashion to Ge(IV) by two N atoms, though in water solutions Ge rather coordinates with oxygen-containing organic molecules, such as malic acid in complex anion [Ge(OH)(HMal)₂]⁻ (**2**). The big interest also represents the differences in crystal structures of synthesized

complexes: three-dimensional net, in the cavities of which uncoordinated 1,10'-phenanthroline molecules are located in **1**, and fiber structure of alternating topological isomeric cations and anions A and B in **2**.

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