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Absolute structure determination of (2*R*,1′*S*)-2-(1′-benzyl-2′-hydroxyethylamino)-4-phenylbutanoic acid

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Abstract

Crystallization-induced asymmetric transformation was employed to prepare a labile γ-oxo-α-aminoacid (**3**) with a new stereogenic center in high diastereomeric and enantiomeric purity. Compound **3** was reduced to a stable compound, (2*R*,1′*S*)-2-(1′-benzyl-2′-hydro-hydroxyethylamino)-4-phenylbutanoic acid (**4**), which crystallizes in space group $P2_1$. Upon deprotonation, **4** becomes a tridentate monoanionic chelating ligand, $\mathbf{4}^{-H}$, which reacts with copper nitrate yielding $[Cu(\mathbf{4}^{-H})(H_2O)_2]NO_3{\cdot}H_2O$ (**5**). Complex **5** crystallizes in space group $P2_1$ and has a rare composition among crystallographically characterized mononuclear five-coordinate transition metal complexes. The absolute structure determination of **5** allowed by inference the assignment of absolute configuration to compound **3**.

Keywords: Unnatural amino acids; Absolute configuration; Crystallization-induced asymmetric transformation; Copper(II) complex

1. Introduction

The synthesis of unnatural amino acids still remains a challenge for organic chemists trying to prepare enantio- and diastereomerically pure derivatives in the simplest and most inexpensive ways. In this connection, crystallization-induced asymmetric transformation (CIAT) is a promising method [1]. The conjugate addition of enantiomerically pure 1-phenylethylamines on the aroylacrylic acids using CIAT conditions has been applied recently to the synthesis of optically pure homophenylalanines [2], and derivatives of *syn*-γ-hydroxy-α-amino-γ-phenylbutanoic acids [3]. These results prompted us to study the stereoselectivity of addition of easily accessible chiral amino alcohols to aroylacrylic acids [4]. An example of (*S*)-phenylalaninol (**2**) is given in Scheme 1. The absolute configuration of the newly built stereogenic centre of the adduct (**3**) could not be assigned by the usual spectroscopic methods. Moreover, the γ-oxo-α-aminoacid (**3**) is unstable both in alkaline and neutral media and its crystallization leads to a significant epimerisation and decomposition. Fortunately, after removal of the activating carbonyl group we were able to prepare a stable amino acid, (2*R*,1′*S*)-2-(1′-benzyl-2′-hydroxy-ethylamino)-4-phenylbutanoic acid, (**4**) with negligible epimerisation. In order to determine its absolute structure, crystals suitable for X-ray analysis have to be grown. Crystallization of compound **4** is difficult and usually yields very thin hair-like crystals. However, after the complexation of **4** with copper(II), suitable crystals for X-ray study were obtained and the absolute structure of the formed complex was determined and by inference, the absolute structure of **4**. Later, crystals of compound **4** of sufficient quality were obtained, too. Syntheses, crystal structures and spectroscopic characterization of **4** and its copper complex $[Cu(\mathbf{4}^{-H})(H_2O)_2]NO_3{\cdot}H_2O$ (**5**) are included in the present study.

2. Experimental

2.1. General

Melting points were obtained using a Kofler hot plate and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter with a water-jacketed 10 cm

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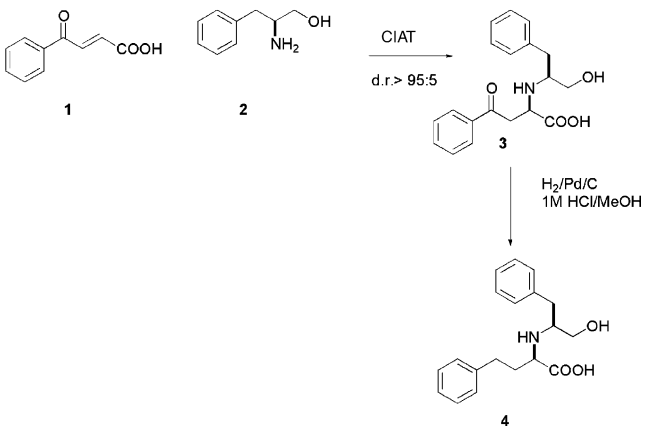


1 2 3 4

Scheme 1.

cell at the wavelength of sodium line D ($\lambda = 589$ nm). Specific rotations are given in units of 10^{-1} deg cm^2 g^{-1} and concentrations are given in g/100 ml. ^{1}H-NMR spectra were recorded on a Varian VXR-300 (299.94 MHz) spectrometer. Chemical shifts (δ) are quoted in ppm and are referenced to residual CH_3OH ($\delta_H = 3.34$ ppm for 299.94 MHz), used as internal reference. Coupling constants (J) are recorded in Hertz. Abbreviations with quotation marks mean that the signal frequency is different from the theoretically predicted one. H-A, H-B mean the signals of magnetically nonequivalent CH_2 protons. ^{13}C NMR spectra were recorded on a Varian VXR-300 (75.43 MHz) spectrometer. Chemical shifts are quoted in ppm and are referenced to the central resonance of CD_3OD ($\delta_C = 49.0$ ppm for 75.43 MHz). Infrared spectra were recorded on a Nicolet 750 FTIR spectrophotometers as KBr pellets.

2.2. Preparation of (2R,1′S)-2-(1′-benzyl-2′-hydroxyethylamino)-4-phenylbutanoic acid (*4*)

Amino acid **3** (1.96 g; 6 mmol) was dissolved in mixture of methanol (90 ml) and 1 M HCl (150 ml). Thereafter the catalyst (10% Pd/C) was added (0.40 g; 20 mol %). The suspension was stirred under H_2 (1.1 atm.) for one day. The catalyst was filtered off and washed with 1% HCl (50 ml). The mixture was partially concentrated under reduced pressure. The pH of the remaining solution is adjusted to 5.0–5.5 with 2N NaOH. The precipitate was filtered off, washed with Et_2O and dried to afford 1.85 g (98%) of amino acid **4** (d.r. > 95:5) as a white solid. An analytical sample was obtained by recrystallization from EtOH with several drops of water: m.p. 212–213 °C, $[\alpha]_D^{20} - 53$ (THF/1 M HCl = 4/1; c 0.6). ^{1}H-NMR (300 MHz; CD_3OD, DCl/TMS): 7.20–7.40 (m, 10H, 2 × Ph), 4.08 (t, 1H, $J = 6.3$, H2), 3.73 (dd, 1H, $J_{3A,3B} = 12.0, J_{3A,4} = 3.3$, H3A), 3.64 (dd, 1H, $J_{3A,3B} = 12.0$, $J_{3B,4} = 5.4$, H3B), 3.51 (m, 1H, H4), 3.16 (dd, 1H, $J_{5A,5B} = 13.5, J_{4,5A} = 5.1$, H5A), 3.03 (dd, 1H, $J_{5A,5B} = 13.5$,

Table 1
Crystal data and structure refinement for **4** and **5**

	4	**5**
Empirical formula	$C_{19}H_{23}NO_3$	$C_{19}H_{28}CuN_2O_9$
Formula weight	313.38	491.97
Temperature (K)	298(2)	302(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions	$a = 10.959(2)$ Å	$a = 6.190(1)$ Å
	$b = 5.972(1)$ Å	$b = 9.046(1)$ Å
	$c = 13.033(2)$ Å	$c = 20.515(2)$ Å
	$\beta = 92.360(2)°$	$\beta = 90.915(2)°$
Volume (Å^3), Z	852.2(2), 2	1148.5(2), 2
Density (calculated) (Mg m^{-3})	1.221	1.423
Absorption coefficient (mm^{-1})	0.082	1.001
$F(000)$	336	514
Crystal size (mm^3)	0.16 × 0.07 × 0.04	0.32 × 0.14 × 0.07
θ range for data collection, deg	1.86–23.25°	1.99–23.26°
Limiting indices	$-12 \le h \le 11$, $-6 \le k \le 4$, $-13 \le l \le 14$	$-6 \le h \le 6$, $-9 \le k \le 10$, $-22 \le l \le 19$
Reflections measured	3785	5022
Independent reflections	1939 [R(int) = 0.0566]	3206 [R(int) = 0.0251]
Observed reflections [$I > 2\sigma(I)$]	1223 [$R_{int} = 0.0813$]	3010 [$R_{int} = 0.0287$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1939/1/209	3206/1/283
Goodness of fit on F^2	0.882	1.033
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0451$, $wR2 = 0.0796$	$R1 = 0.0326$, $wR2 = 0.0869$
R indices (all data)	$R1 = 0.0914$, $wR2 = 0.0906$	$R1 = 0.0353$, $wR2 = 0.0886$
Largest diff. peak and hole	0.121 and −0.143 e Å^{-3}	0.245 and −0.183 e Å^{-3}

$J_{4,5B} = 9.5$, H5B), 2.82–2.95 (m, 1H, H13A), 2.65–2.80 (m, 1H, H13B), 2.30 (m, 2H, H12); ^{13}C-NMR (75 MHz; CD_3OD, DCl/TMS): 171.3 (C1); 141.1, 137.2, 130.3, 130.0, 129.7, 129.5, 128.4, 127.5 (C–Ar); 62.6, 60.1, 59.0 (C2, C4, C3); 34.6, 32.9, 32.1 (C12, C13, C5); IR (KBr disk): 3366(s), 3085(m), 3063(m), 3032(m), 3010(w), 2961(m), 2925(m), 2877(m), 2613(w), 2582(w), 1636(s), 1608(vs), 1587(w), 1570(vs), 1496(m), 1475(vw), 1456(m), 1447(vw), 1434(w), 1394(s), 1383(m), 1355(m), 1339(m), 1329(w), 1314(w), 1307(w), 1285(vw), 1272(w), 1235(w), 1221(m), 1205(vw), 1178(w), 1160(w), 1110(m), 1064(m), 1059(w), 1030(s), 1009(sh), 983(vw), 964(w), 940(w), 906(vw), 909(w), 873(w), 816(w), 783(w), 755(m), 740(m), 696(vs), 643(w), 629(vw), 608(m), 576(w), 535(m), 503(m), 453(w), 414(w).

2.3. Preparation of $[Cu(\mathbf{4}^{-H})(H_2O)_2]NO_3{\cdot}H_2O$ (**5**)

To a solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.020 g; 0.09 mmol) in methanol (2 ml) was added **4** (0.012 g; 0.02 mmol) dissolved in 2 ml of THF/H_2O = 10:1 at ambient temperature. No colour change was observed. After three weeks, pale blue needles of **5** suitable for X-ray experiment were isolated. Yield: 0.014 g (74%). Elemental analysis, found (calcd for $C_{19}H_{28}CuN_2O_9$): C, 45.53 (46.39); H, 5.75 (5.74); N, 5.72 (5.69)%. IR (KBr disk): ≈3460(sh), 3278(m), 3170(m), 3086(m), 3062(m), 3026(m), 3000(w), 2978(m), 2949(m), 2933(m), 2922(m), 2864(m), 1682(s), 1653(m), 1628(s), 1603(m), 1585(m), 1541(w), 1522(vw), 1497(m), 1473(vw), 1456(m), 1431(m), 1407(sh), 1385(vs), 1360(m), 1342(m), 1335(m), 1325(m), 1271(vw), 1253(sh), 1230(w), 1209(vw), 1192(w), 1155(vw), 1120(w), 1097(vw), 1086(vw), 1068(m), 1041(m), 1026(m), 1005(w), 989(w), 953(vw), 922(vw), 906(vw), 889(vw), 850(vw), 823(w), 779(m), 746(s), 737(m), 698(s), 629(w), 602(w), 582(vw), 573(w), 501(w), 472(vw), 438(w), 405(vw).

2.4. Crystallography

Single crystals of **4** suitable for X-ray crystalloghraphic studies were obtained as colourless needles from THF/H_2O (10:1) solution by slow evaporation. Crystals of **5** were obtained directly from the reaction mixture. The crystals were mounted on the tip of glass fiber with epoxy glue. Single crystal analyses were carried out on a Bruker SMART 1K CCD diffractometer. The frame data were acquired with the SMART [5] software using Mo Kα radiation ($\lambda = 0.71073$ Å). Final values of the cell parameters were obtained from least-squares refinement of the positions of 911 reflections. A total of 1271 45-s frames were collected in three sets with 0.3° ω-scan for both structures. The frames were then processed using the SAINT software [6] to give the *hkl* file corrected for Lorentz and polarization effects. No absorption correction was applied. The structures were solved by direct method using the SHELX-90 [7] program and refined by least-squares method on F^2, SHELXTL-93 [8], incorporated in SHELXTL, Version 5.1 [9]. The initial E-maps yielded all non-hydrogen atom positions. Hydrogen atoms were geometrically positioned and left riding on their parent atoms during structure refinement. All non-hydrogen atoms were refined anisotropically. Table 1 summarizes the structural and refinement parameters. A list of important distances and angles is given in Table 2.

Table 2
Selected bond lengths (Å) and angles (°) for **5** and **4**

Cu(1)–O(5)	1.935(3)	
Cu(1)–O(1)	1.962(2)	
Cu(1)–O(4)	1.977(3)	
Cu(1)–N(1)	2.014(3)	
Cu(1)–O(3)	2.179(3)	
O(1)–C(1)	1.292(4)	1.255(4)
O(2)–C(1)	1.211(4)	1.255(5)
O(3)–C(3)	1.432(5)	1.420(5)
N(1)–C(4)	1.482(5)	1.515(4)
N(1)–C(2)	1.497(4)	1.498(4)
C(1)–C(2)	1.516(5)	1.535(5)
C(2)–C(12)	1.533(5)	1.526(5)
C(3)–C(4)	1.521(5)	1.518(5)
C(4)–C(5)	1.547(5)	1.526(5)
C(5)–C(6)	1.498(6)	1.507(5)
C(12)–C(13)	1.527(5)	1.518(5)
C(13)–C(14)	1.524(5)	1.504(5)
O(5)–Cu(1)–O(1)	93.37(12)	
O(5)–Cu(1)–O(4)	86.88(13)	
O(1)–Cu(1)–O(4)	159.32(15)	
O(5)–Cu(1)–N(1)	177.05(12)	
O(1)–Cu(1)–N(1)	83.69(10)	
O(4)–Cu(1)–N(1)	95.81(12)	
O(5)–Cu(1)–O(3)	96.16(12)	
O(1)–Cu(1)–O(3)	103.08(11)	
O(4)–Cu(1)–O(3)	97.44(15)	
N(1)–Cu(1)–O(3)	84.69(11)	
C(1)–O(1)–Cu(1)	114.0(2)	
C(3)–O(3)–Cu(1)	103.2(2)	
C(4)–N(1)–Cu(1)	108.8(2)	
C(2)–N(1)–Cu(1)	104.2(2)	
C(4)–N(1)–C(2)	114.2(3)	115.2(3)
O(2)–C(1)–O(1)	124.1(3)	126.9(4)
O(2)–C(1)–C(2)	120.1(3)	115.1(4)
O(1)–C(1)–C(2)	115.8(3)	118.0(4)
N(1)–C(2)–C(1)	108.2(3)	108.0(3)
N(1)–C(2)–C(12)	111.4(3)	110.8(3)
C(1)–C(2)–C(12)	107.6(3)	110.3(3)
O(3)–C(3)–C(4)	111.3(3)	113.2(3)
N(1)–C(4)–C(3)	109.2(3)	109.3(3)
N(1)–C(4)–C(5)	114.1(3)	110.2(3)
C(3)–C(4)–C(5)	108.6(3)	114.3(3)
C(6)–C(5)–C(4)	117.1(3)	112.3(3)
C(11)–C(6)–C(5)	121.4(4)	120.5(4)
C(7)–C(6)–C(5)	119.1(4)	121.2(5)
C(13)–C(12)–C(2)	113.8(3)	115.9(3)
C(14)–C(13)–C(12)	111.2(3)	111.4(3)
C(19)–C(14)–C(13)	121.3(4)	121.5(4)
C(15)–C(14)–C(13)	121.1(4)	121.2(4)

3. Results and discussion

The title compound **4** was prepared in high diastereomeric excess using an inexpensive and efficient CIAT. The core principle of CIAT methodology is the existence of dynamic equilibrium between the isomers in solution. Thus the adduct **3** is sufficiently stable only in solid state. In quest of the stabilization of the newly formed stereogenic centre at C2, the further transformation to the more stable derivate **4** has been realized. The NMR spectra of the reduced derivate **4**, taken in CD_3OD/DCl, show some extend of rigidity, owing to intramolecular hydrogen bonds. The signals of the three CH_2 groups at C3 and both benzylic positions are magnetic non-equivalent and with well-developed splitting (see experimental). However, neither the measured splitting constants in ^{1}H-NMR, nor the other NMR experiments did allow interpretation of the configuration on the newly formed stereogenic centre at C2.

The complete molecular structure of **4** was obtained from the X-ray crystallographic study (Fig. 1). Moreover, it was possible to determine the absolute configuration using the modification of compound **4** to complex structure with a heavier atom. We have decided to use **4** as an organic ligand in a complexation reaction with a transition metal. Compound **4** has four potential donor atoms: two carboxylic and one hydroxide oxygens and one secondary amino nitrogen. Copper(II) nitrate was chosen as a source of a central atom. The choice of Cu(II) relies on its plasticity towards different coordination environments [10], and the affinity of copper(II) for O- as well as N-ligands. Nitrate was used because of its poor complexation to Cu(II). An excess

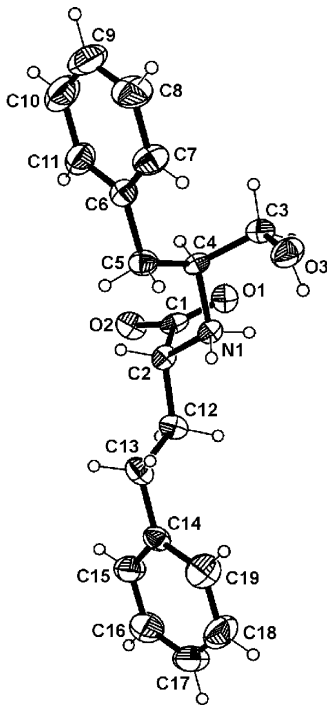


Fig. 1. Molecular structure and atom labeling scheme for **4**. Thermal ellipsoids shown at 30% probability.

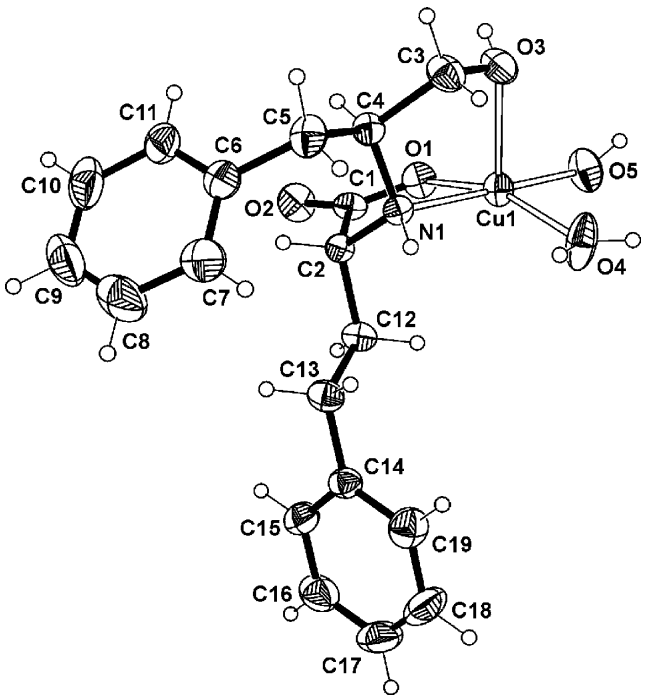


Fig. 2. Molecular structure and atom labeling scheme for **5**. Thermal ellipsoids shown at 30% probability.

of Cu in the complexation reaction results in 1:1 metal to ligand complex formation. Under the applied conditions, ligand **4** was able to display its full complexation ability. In the product **5**, it acts as a tridentate chelating ligand using nitrogen, hydroxide oxygen and one oxygen from the carboxylic group to coordinate copper (Fig. 2) in a distorted square-pyramidal manner. Compound **5** is chiral, as the ligand **4** is. Since, the absolute structure of **5** was readily determined from the X-ray study, the absolute structure of **4** was inferred.

All inter-atomic distances found in **4** are within typical ranges. The C–C bond lengths (1.504(5)–1.535(5) Å) are typical for single C–C bond and the shorter C–C contacts (1.350(8)–1.389(6) Å) belong to conjugated benzene rings. The carboxylic group is deprotonated with equal C–O bond lengths (1.255(4) and 1.255(5) Å) indicating electron delocalisation. The secondary amine N1 atom is protonated with C–N contacts (1.498(4) and 1.515(4) Å), typical of single bonds. The absolute configuration on the chiral atom C2 is *R* while on C4 it is *S*. Three hydrogen bonds (Table 3), in which secondary amine, hydroxyl and carboxyl groups are involved, link molecules forming a linear polymeric structure along the *b*-axis.

Table 3
Specified hydrogen bonds for **4**

D–H	H···A	D···A	<(DHA)	D–H···A
0.82	2.05	2.778(4)	147.6	O3–H3···O1 $(x, y+1, z)$
0.90	1.99	2.838(4)	156.0	N1–H1A···O1 $(-x, y+1/2, -z)$
0.90	1.87	2.766(4)	173.9	N1–H1B···O2 $(x, y+1, z)$

Table 4
Specified hydrogen bonds for **5**

D–H	H···A	D···A	<(DHA)	D–H···A
0.77	1.96	2.717(4)	166.3	O3–H1O3···O6 ($-x+1, y-1/2, -z+1$)
0.82	2.05	2.736(4)	140.5	O4–H1O4···O1 ($x+1, y, z$)
0.83	1.99	2.774(4)	157.3	O4–H2O4···O7 ($x+1, y-1, z$)
0.82	1.87	2.663(4)	162.7	O5–H1O5···O6 ($x, y-1, z-1$)
0.83	1.89	2.700(4)	167.6	O5–H2O5···O7 ($x, y-1, z$)
0.78	2.25	2.815(5)	129.4	O6–H1O6···O9 ($-x+1, y+1/2, -z+1$)
0.83	1.97	2.761(5)	159.5	O6–H2O6···O8 ($x+1, y, z+1$)
0.70(4)	2.23(4)	2.926(4)	172(4)	N1–H1···O2 ($x+1, y, z$)

The molecular structure of coordinated compound **4** is only slightly different from the free molecule. Interatomic contacts are almost the same with minor differences in bond lengths for donor atoms, but a different conformation has been adopted to facilitate chelation to Cu. In the copper(II) complex **5**, compound **4** exists as a deprotonated mono-anionic ligand ($\mathbf{4}^{-H}$) loosing its Zwitterionic character. This is reflected in the shortening of N1–C4 bond (1.482(5) Å), (in spite the fact that the lone electron pair on N1 was used towards coordination) and in C–O bond length differentiation within the carboxylic group. The C1–O1 distance becomes longer (1.292(4) Å) and C1–O2 shorter (1.211(4) Å) indicating localization of the charge on O1 atom. The hydroxylic group remains protonated but the C3–O3 distance is slightly elongated (1.432(5) Å) due to Cu1–O3 coordination. Copper(II) is in a distorted square-pyramidal environment, with the basal plane formed by N1 and O1 of $\mathbf{4}^{-H}$ and two coordinated water molecules. The apical position is occupied by O3 from the chelating ligand. The copper atom is lifted 0.183(2) Å above the calculated best fit plane of the basal donor atoms, which is indeed slightly tetrahedraly distorted, as evident from its diagonal angles (N1–Cu1–O5, 177.05(12), O1–Cu1–O4, 159.32(15)°). The apical O3 atom is 2.348(3) Å above the calculated ideal basal plane, deviating by 6.6° from the perpendicular position with respect to Cu1. The complex cation, $[Cu(\mathbf{4}^{-H})(H_2O)_2]^+$, counter-anion, NO_3^- and non-coordinated interstitial water molecule are held together in the crystal structure via a 3D hydrogen bond system, involving all acidic hydrogen atoms (Table 4). Due to carboxylic group presence, complex cations form 1D polymeric chains along the crystallographic a axis via two

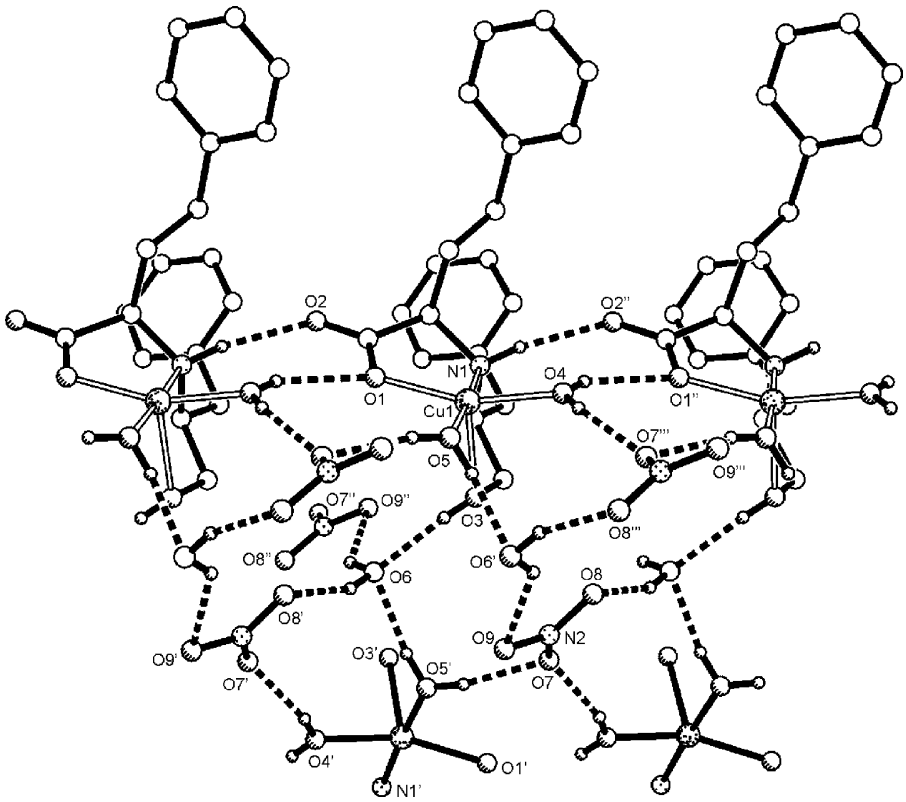
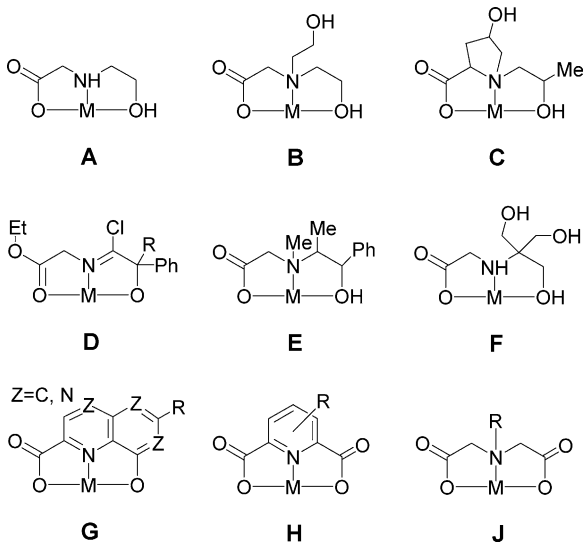


Fig. 3. Packing diagram for compound **5** showing the 3D network of H-bonds. Hydrogen atoms not involved in H-bonding were omitted for clarity.



Scheme 2.

H-bonds (N1–H1···O2 and O4–H1O4···O1). The chain is stabilized by two additional H-bonds provided by O7 of nitrate group (O4–H2O4···O7 and O5–H2O5···O7). The nitrate anion and non-coordinated water molecule form four more H-bonds, which interlink the above mentioned 1D chains into a complicated 3D structure (Fig. 3).

Comparison of IR spectra for both compounds, ligand **4** and the Cu(II) complex **5**, show important differences. In **4**, ν(C–H), ν(N–H), and ν(O–H) vibrations are well resolved, while in **5**, those are superimposed on a broad system of bands, which belong to coordinated and crystal lattice water molecules. Coordination of carboxylic group should cause shifts of both asymmetric and symmetric infrared frequencies of COO group [11]. Strong absorptions at 1394 and 1570 cm^{-1} could be tentatively assigned to $\nu_s(CO_2^-)$ and $\nu_a(CO_2^-)$ for **4**, resulting in 176 cm^{-1} Δ value [$\nu_a(CO_2^-)-\nu_s(CO_2^-)$]. For **5**, $\nu_a(CO_2^-)$ was shifted to 1682 and $\nu_s(CO_2^-)$ to 1385 cm^{-1}, resulting in much greater Δ value (297 cm^{-1}), indicative of the unidentate coordination mode of carboxylate [11]. Frequencies in other regions of the recorded infrared spectrum were much less affected by the complexation of **4**, and show negligible shifts.

To the best of our knowledge and to our surprise, the tridentate ligand $\mathbf{4}^{-H}$ represents a rare motif among tridentate ligands in crystallographically characterized [12] transition metal complexes (A in Scheme 2). Upon coordination, it forms two five-membered metallacycles with central secondary amino N donor and side hydroxyl and carboxyl O donor atoms. Only six other tridentate ligands (and their derivatives) possessing similar skeletons were found [13–26]. All six differ in their coordination mode. Ligand B coordinates exclusively in *fac*-mode [13–15], ligands E and F adopt both *fac*- and/or *mer*-type of coordination [19–22], but ligands C, D, and G form only *mer*-complexes [16–18,23–26]. Among them, only two five-coordinate complexes were found, both are Cu(II) complexes - one is polymeric [21], while the other one is trinuclear [20]. In both complexes, tridentate ligands form part of basal plane of distorted square pyramid unlike the studied complex **5**, in which $\mathbf{4}^{-H}$ is in a *fac*-mode. Only few more five-coordinate Cu(II) complexes with different tridentate ONO ligands (H and J in Scheme 2) suitable for comparison with **5** are known [27–32]. Both ligand types coordinate in *mer*-mode and the complexes are square-pyramidal. This only stresses the uniqueness of ligand $\mathbf{4}^{-H}$, inspite of its simple architecture.

4. Conclusions

The absolute structure of the title compound was elucidated after the crystal structure of its copper(II) complex was studied. Upon deprotonation, **4** becomes a tridentate monoanionic chelating ligand, $\mathbf{4}^{-H}$, capable of adopting a rare coordination motif. Complex [Cu($\mathbf{4}^{-H}$)-$(H_2O)_2$]NO_3·H_2O (**5**) is indeed the first crystallographically described mononuclear five-coordinate transition metal complex of the type [M(ONO)LL′], where (ONO) is a tridentate chelating ligand with O-carboxyl, N-amino, O-hydroxo donor atoms and L, L′ any monodentate ligands.

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Appendix A

CCDC 229987 and 229988 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033).

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