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A tetrazol-5-yl analogue of glycine, 5-ammoniomethyl-1*H*-tetrazolide, and its copper(II) complex

Alexander S. Lyakhov,* Sergei V. Voitekhovich, Ludmila S. Ivashkevich and Pavel N. Gaponik

Research Institute for Physico-Chemical Problems, Belarusian State University, Leningradskaya Street 14, Minsk 220030, Belarus
Correspondence e-mail: lyakhov@bsu.by

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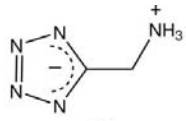
A nonclassical tetrazole isostere of glycine, *viz*. zwitterionic 5-ammoniomethyl-1*H*-tetrazolide, $C_2H_5N_5$, (I), crystallizes in the chiral $P3_1$ space group, similar to γ-glycine. The crystal packing of (I) is determined by a set of classical hydrogen bonds, forming a three-dimensional network that is practically the same as that in γ-glycine. The Cu^{II} complex of (I), poly-[[bis(μ_2-5-aminomethyl-1*H*-tetrazolido-$\kappa^3N^1,N^5:N^4$)copper(II)] dihydrate], $\{[Cu(C_2H_4N_5)_2]\cdot 2H_2O\}_n$, (II), is a layered coordination polymer formed as a result of tetrazole ring bridges. The Cu^{II} cations lie on inversion centres, are surrounded by four anions and adopt elongated octahedral coordination. Water molecules are located in the interlayer space and connect the layers into a three-dimensional network *via* a system of hydrogen bonds.

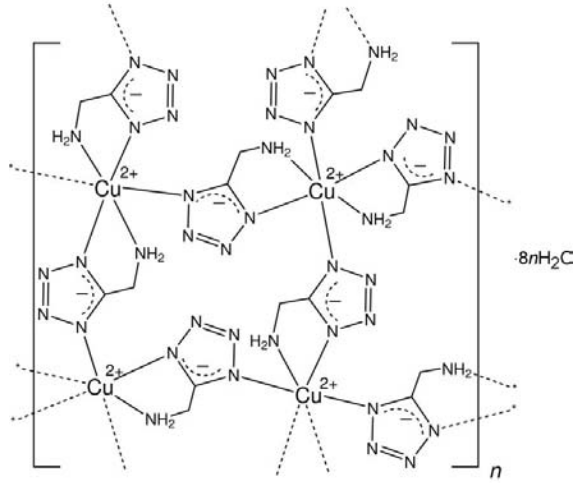
Comment

The tetrazole ring is extensively used in molecular design and in the synthesis of modified amino acids and peptidomimetics, because the tetrazol-5-yl group, $-CN_4H$, is a nonclassical isostere for the carboxylic acid group, –COOH. These functional groups have similar chemical properties and may be interchangeable, resulting in compounds with similar biological properties. Moreover, the tetrazole-1,5-diyl group, $-CN_4-$, is a *cis*-amide –C(=O)N– surrogate (Ostrovskii *et al.*, 2008). In particular, 5-aminomethyl-1*H*-tetrazole and its derivatives form an interesting class of tetrazole analogues of natural α-amino acids. Moreover, they are the precursors of dipeptides, attractive as catalysts for the direct asymmetric intermolecular aldol reaction (Zheng, Li *et al.*, 2006). However, very little has appeared in the literature concerning their structure. Only a few examples of 5-aminomethyl-1*H*-tetrazole derivatives have been structurally characterized. These are zwitterionic 5-piperidiniomethyl-1*H*-tetrazolide (Lyakhov *et al.*, 2003), 1-phenyl-5-piperidinomethyl-1*H*-tetrazole (Lyakhov *et al.*, 2004) and (*S*)-*N*-(1*H*-tetrazol-5-ylmethyl)pyrrolidine-2-carboxamide dihydrate (Zheng, Zhang *et al.*, 2006). In spite of interest in the coordination chemistry of these compounds, mainly potentiometric and spectroscopic (UV–vis, circular dichroism and electron paramagnetic resonance) studies have been undertaken (Lodyga-Chruscinska *et al.*, 2006, and references therein), and only the structure of a copper(II) chloride complex with *N*,*N*-dimethyl-1-(1-methyl-1*H*-tetrazol-5-yl)methanamine has been reported (Ivashkevich *et al.*, 2002).

The present paper is concerned with 5-methylaminotetrazole existing in the crystal in zwitterionic form as 5-ammoniomethyl-1*H*-tetrazolide, (I). The compound is a tetrazol-5-yl analogue of the simplest α-amino acid, glycine. We present here also a Cu^{II} complex of (I), namely poly[[bis(μ_2-5-aminomethyl-1*H*-tetrazolido-$\kappa^3N^1,N^5:N^4$)copper(II)] dihydrate], (II). It should be noted that (I) was synthesized 50 years ago (McManus & Herbst, 1959). As to its metal derivatives, they are hitherto unknown.



(I)



(II)

Compound (I), whose molecules are achiral in solution, crystallizes in the enantiomeric pair of chiral space groups $P3_1$ and $P3_2$. It may be expected that the distribution of the crystalline product between the two space groups is essentially statistical.

Zwitterions (I) are produced when the H atom of the tetrazole ring is transferred to the amine group N atom (Fig. 1). As a consequence, the tetrazole ring is rather symmetrical (Table 1). The C5—N1 and C5—N4 bond lengths are practically the same, as are the N1—N2 and N3—N4 bonds. The N2=N3 bond is the shortest in the ring. The tetrazole ring is essentially planar, to within 0.0021 (10) Å, so the ring symmetry is close to C_{2v}. The obtained ring geometry corresponds to charge delocalization in the N1—C5—N4 fragment.

All H atoms of the NH_3 groups are involved in classical intermolecular hydrogen bonding (Table 2). Bifurcated

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hydrogen bonds [N7—H7*B*···N2^{ii} and N7—H7*B*···N3^{ii}; symmetry code: (ii) x, y, $z+1$] connect the zwitterions into chains running along the *c* axis. These chains are bonded through lateral hydrogen bonds [N7—H7*A*···N1^{i} and N7—H7*C*···N4^{iii}; symmetry codes: (i) $-y$, $x-y$, $z+\frac{1}{3}$; (iii) $-y$, $x-y-1$, $z+\frac{1}{3}$] to form a three-dimensional network (Fig. 2).

It is of interest to compare the structure of (I) with that of glycine, which crystallizes in three polymorphic forms, α ($P2_1/n$), β ($P2_1$) and γ ($P3_1$), reported previously (Boldyreva *et al.*, 2003, and references therein). Analysis shows that the structure of (I) is very close to that of γ-glycine. Both compounds are achiral but crystallize in the same chiral space group $P3_1$ ($P3_2$). In (I), the values of the cell dimensions are somewhat greater than those in γ-glycine, in agreement with the sizes of the molecules. The crystal packing is practically the same in the two compounds, being determined by similar hydrogen bonds [N—H···N in (I) and N—H···O in γ-glycine].

The asymmetric unit of complex (II) is shown in Fig. 3. The Cu^{II} cations lie on inversion centres and are surrounded by four anions to form an elongated octahedral coordination (Table 3). The tetrazole ring N4 atoms of two tetrazolide anions lie in axial positions of the octahedron. Two other anions in the Cu^{II} environment are coordinated in a bidentate fashion *via* atoms N1 and N7, occupying equatorial sites of the octahedron. Within 3σ, the tetrazole ring bond lengths are the same as those in (I). Moreover, the complexing has practically no influence on the C5-substituent conformation. Complex (II) is a layered coordination polymer, with layers parallel to the *bc* plane. Within a layer, each ligand acts as a bridge between adjacent Cu^{II} cations, separated by *ca* 6.35 Å (Fig. 4). Water molecules, located in the interlayer space, connect the layers into a three-dimensional network *via* a system of hydrogen bonds, each water molecule acting as both a donor and an acceptor of H atoms (Fig. 5 and Table 4). Although the water molecules are not coordinated to the Cu atoms, the solvent molecules play an important role in the crystal packing. According to the thermal analysis data, the complex shows high thermal stability and does not reveal water loss up to decomposition, which takes place as an exothermal process at 514 K. Note that the only reported Cu^{II} complex of glycine (Casari *et al.*, 2004, and references therein) is different from (II) in composition and crystal structure, including the Cu^{II} coordination environment, polymeric structure and hydrogen-bond system.

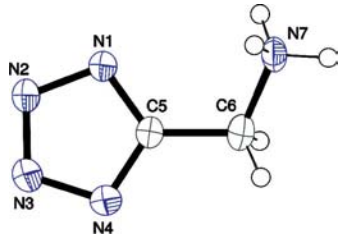

Figure 1
The zwitterion in the crystal structure of (I), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

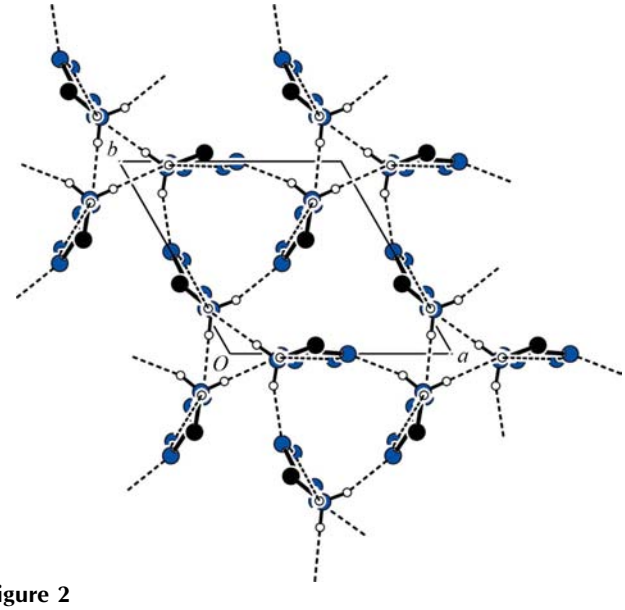

Figure 2
The crystal structure of (I), viewed along the *c* axis. Dashed lines indicate hydrogen bonds. The methylene H atoms have been omitted for clarity.

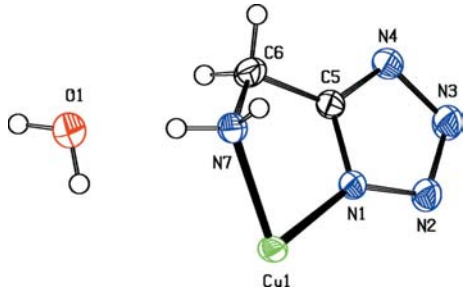

Figure 3
The atom numbering in the asymmetric unit of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

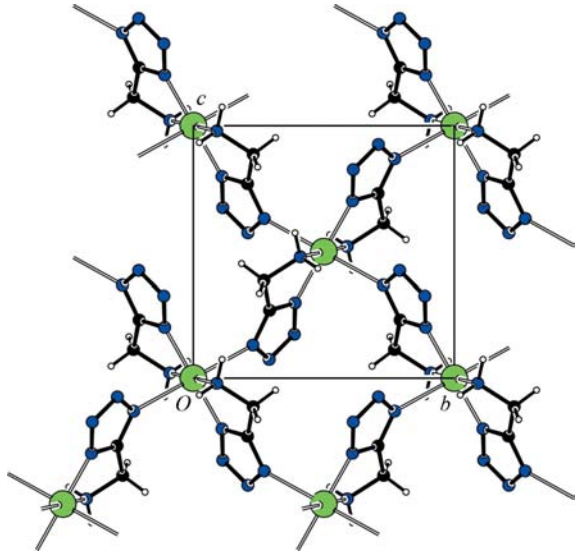

Figure 4
A coordination layer in the structure of (II), parallel to the *bc* plane.

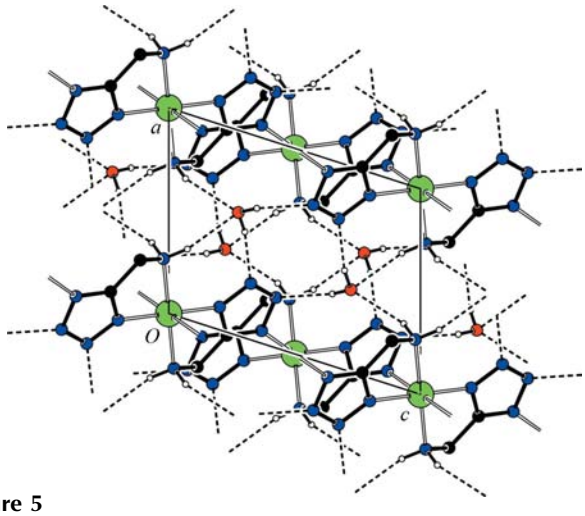

Figure 5
The crystal structure of (II), viewed along the *b* axis. Dashed lines represent hydrogen bonds. Only H atoms participating in hydrogen bonds are shown.

Experimental

5-Chloromethyltetrazole (1 g, 8.4 mmol), synthesized from chloroacetonitrile, sodium azide and aluminium chloride according to the method reported by Vereshchagin *et al.* (2006), was dissolved in 25% aqueous ammonia (5 ml). The resulting solution was kept at room temperature for 1 d and evaporated under vacuum. The residue was recrystallized from a water–ethanol solution (10:1), yielding colourless crystals of (I) (yield 85%, 1.1 g; m.p. 560–561 K). Analysis found: C 24.31, H 5.11, N 70.71%; calculated for $C_2H_5N_5$: C 24.24, H 5.09, N 70.67%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.10 (*s*, 2H, CH_2). ^{13}C NMR (125 MHz, DMSO-d_6): δ 35.2 (CH_2), 156.1 ($C_{tetrazole}$). To obtain (II), a mixture of water (20 ml), 5-aminomethyltetrazole (99 mg, 1 mmol) and copper(II) oxide (40 mg, 0.5 mmol) was refluxed for 15 h. The resulting solution was filtered and, after slow cooling, blue crystals of (II) suitable for X-ray analysis were obtained (yield 50%, 78 mg). Analysis found: C 16.39, H 4.02, N 47.60%; calculated for $C_4H_8CuN_{10}$: C 16.24, H 4.09, N 47.36%.

Compound (I)

Crystal data

$C_2H_5N_5$
M_r = 99.11
Hexagonal, $P3_1$
a = 7.3048 (11) Å
c = 6.9003 (14) Å
V = 318.87 (9) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 294 K
0.52 × 0.34 × 0.32 mm

Data collection

Nicolet R3m four-circle diffractometer
1076 measured reflections
624 independent reflections
611 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
2 standard reflections every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.078
S = 1.11
624 reflections
65 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

N1—C5	1.3284 (16)	N3—N4	1.3479 (17)
N1—N2	1.3478 (17)	N4—C5	1.3288 (16)
N2—N3	1.2995 (19)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N7—H7A···N1^{i}	0.89	2.07	2.9443 (15)	169
N7—H7B···N2^{ii}	0.89	1.97	2.8417 (18)	168
N7—H7B···N3^{ii}	0.89	2.60	3.3379 (17)	141
N7—H7C···N4^{iii}	0.89	1.97	2.8300 (18)	162

Symmetry codes: (i) $-y, x-y, z+\frac{1}{3}$; (ii) $x, y, z+1$; (iii) $-y, x-y-1, z+\frac{1}{3}$.

Compound (II)

Crystal data

$[Cu(C_2H_4N_5)_2]\cdot 2H_2O$
M_r = 295.79
Monoclinic, $P2_1/c$
a = 7.0452 (18) Å
b = 8.907 (2) Å
c = 9.059 (2) Å
β = 107.80 (2)°
V = 541.3 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.03 mm^{-1}
T = 294 K
0.38 × 0.34 × 0.28 mm

Data collection

Nicolet R3m four-circle diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.483, T_{max} = 0.563
1681 measured reflections
1590 independent reflections
1406 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
2 standard reflections every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.076
S = 1.11
1590 reflections
85 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Cu1—N1	2.0075 (12)	Cu1—N4^{i}	2.4605 (14)
Cu1—N7	2.0488 (13)		

Symmetry code: (i) $-x, y-\frac{1}{2}, -z-\frac{1}{2}$.

For (I), the systematic absences permitted the space groups $P3_1$ and $P3_2$. In the absence of significant resonant scattering, it was impossible to distinguish between these enantiomeric space groups. In view of this, Friedel pairs were merged and the space group $P3_1$ was used. All H atoms of (I) were placed in calculated positions (C—H = 0.97 Å and N—H = 0.89 Å) and refined using a riding model [U_{iso}(H) = 1.2U_{eq}(parent)]. In (II), water H atoms were located from a difference map and refined with distance restraints for the O—H [0.88 (2) Å] and H···H [1.41 (2) Å] distances [U_{iso}(H) = 1.5U_{eq}(O)]. The remaining H atoms of (II) were placed in calculated positions (C—H = 0.97 Å and N—H = 0.90 Å) and refined using a riding model [U_{iso}(H) = 1.2U_{eq}(parent)].

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N7—H7A···O1	0.90	2.22	3.037 (2)	150
N7—H7B···O1^{ii}	0.90	2.23	3.037 (2)	149
O1—H1A···N2^{iii}	0.85 (2)	2.01 (2)	2.842 (2)	167 (3)
O1—H1B···N3^{iv}	0.86 (2)	2.14 (2)	2.969 (2)	163 (3)

Symmetry codes: (ii) $-x+1, -y, -z$; (iii) $-x, -y, -z$; (iv) $x+1, y, z+1$.

For both compounds, data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software* for (I) and *OMNIBUS* (Gałdecka, 2002) for (II); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3037). Services for accessing these data are described at the back of the journal.

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