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1:1 Adduct of (*S*,*S*)-4-amino-3,5-bis-(1-hydroxyethyl)-1,2,4-triazole with (*S*,*S*)-1,2-bis(2-hydroxypropionyl)-hydrazine stabilized by eight hydrogen bonds

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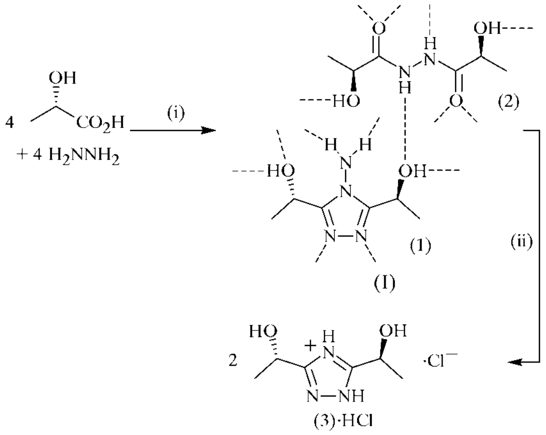
The structure of the cocrystallized 1:1 adduct of (*S*,*S*)-4-amino-3,5-bis(1-hydroxyethyl)-1,2,4-triazole and (*S*,*S*)-1,2-bis(2-hydroxypropionyl)hydrazine, $C_6H_{12}N_4O_2{\cdot}C_6H_{12}N_2O_4$, has tetragonal symmetry. All eight O- and N-bound H atoms are involved in intermolecular hydrogen bonds, resulting in infinite zigzag chains of the triazole molecules, with the hydrazine molecules filling the gaps between the chains and completing a three-dimensional hydrogen-bonded array.

Comment

Triazoles are of special interest as ligands for transition metal ions because of their ability to mediate magnetic exchange and the fact that they can lead to spin-crossover complexes of iron (Klingele *et al.*, 2005; Haasnoot, 2000; Kahn, 1999). We were the first to structurally characterize Schiff base macrocyclic complexes which incorporated triazole moieties in the macrocycle framework. The resulting dimetallic copper(II), nickel(II), cobalt(II) and cobalt(III) Schiff base macrocyclic complexes feature double triazolate bridging of the metal ions and exhibit interesting structural, reactivity and magnetic properties (Beckmann & Brooker, 2003; Beckmann, Brooker *et al.*, 2003; Beckmann, Ewing & Brooker, 2003; Depree *et al.*, 2003). The dimetallic [2+2] Schiff base macrocyclic complexes were obtained from a metal-ion-templated condensation reaction of the appropriately derivatized triazole head unit (Alonso *et al.*, 1987; de Mendoza *et al.*, 1992) with an appropriately selected diaminoalkane lateral unit.

In our studies we have used, amongst other compounds, 3,5-diacetyl-1*H*-1,2,4-triazole as the head unit (Brandt *et al.*, 2006). This compound is obtained *via* a four-step synthesis (Alonso *et al.*, 1987; de Mendoza *et al.*, 1992). The first step of the published procedure involves heating the reaction mixture to 433 K for 5 h and monitoring the reaction by NMR for the disappearance of open-chain intermediates. However, when following this procedure we found that, even after heating the reaction mixture to 443 K overnight, there is sometimes still an open-chain intermediate, (2), present in an exact 1:1 ratio with the desired triazole, (1) [step (i) in the scheme; 373–443 K, overnight; dashed lines represent hydrogen bonds]. This was indicated by elemental analysis and NMR data and has been confirmed by this study.



Attempts to separate the two products, *viz*. (1) and (2), by fractional crystallization, even by the addition of small amounts of water to provide an alternative to the intermolecular hydrogen bonds present (see below), failed and always resulted in analytically pure samples of a 1:1 mixture of (1) and (2). Interestingly, when using mandelic acid instead of lactic acid we observed no open-chain intermediate; this reaction yielded only the corresponding triazole in good yields (Brandt *et al.*, 2006). Fortunately, the presence of (2) does not disturb the next reaction step [deamination of (1)], so (*S*,*S*)-3,5-bis(1-hydroxyethyl)-1,2,4-triazole, (3), can be obtained in high purity and good yield as the hydrochloride salt [step (ii)

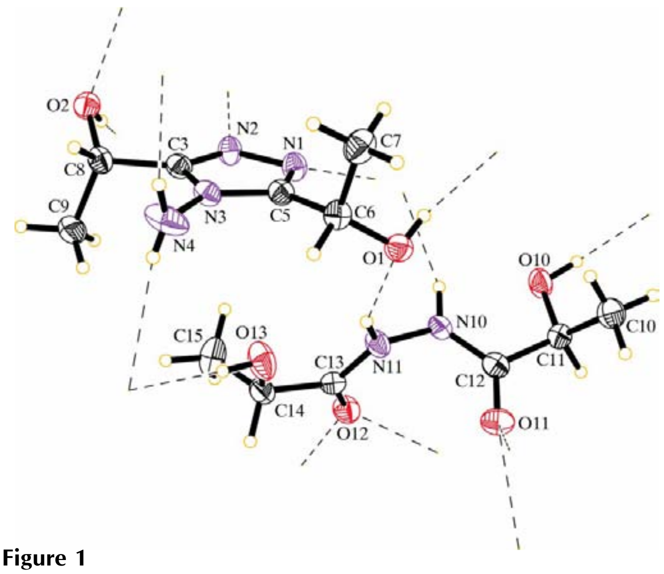


Figure 1
The molecular structure and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds.

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in the scheme; HCl, $NaNO_2$]. Thus, we did not obtain the free triazole directly but instead first isolated the hydrochloric salt, as this has proved to be the best way to separate the triazole from the open-chain compound (*S*,*S*)-1,2-bis(2-hydroxypropionyl)hydrazine, (2).

The structure of the 1:1 adduct, (I), is shown in Figs. 1 and 2, and geometric details are given in Tables 1 and 2. The structure determination confirms the presence of the expected (*S*,*S*)-4-amino-3,5-bis(1-hydroxyethyl)-1,2,4-triazole, (1), and that it has cocrystallized in a 1:1 ratio with the open-chain intermediate (*S*,*S*)-1,2-bis(2-hydroxypropionyl)hydrazine, (2). It is important to note that all of the H atoms on N and O atoms were found in a difference map and their coordinates freely refined.

The N—N single bond in (2), *viz*. N10—N11, is somewhat shorter than those observed in hydrazine (1.46 Å; Collin & Lipscomb, 1951) or in various hydrogen-bonded adducts of hydrazine [*e.g.* 1.46 Å (Liminga & Sorenson, 1967; Liminga, 1967) and 1.43–1.44 Å (Toda *et al.*, 1995)], but is normal compared with those observed in related C—(C═O)—(NH)—(NH)—(C═O)—C compounds [*e.g.* 1.394 (3) Å (Cheng *et al.*, 2006); range observed for 22 such species in the Cambridge Structural Database (Version 5.27, May 2006 update; Allen, 2002) 1.251–1.404 Å, average 1.387 Å]. The torsion angle along the N—N axis in (2) is close to 90° (Table 1). As all of the related compounds are also involved in interesting hydrogen-bonding patterns, and some are cyclic, it is not surprising that the torsion angle along this N—N bond is seen to vary extremely widely. In the compound reported by Cheng *et al.* (2006), the torsion angle is not dissimilar, at 83.1 (2)°.

Within the triazole ring of (1), the N1—N2 distance is somewhat shorter than the N—N single-bond distance observed in hydrazine, but is very close to that observed for N3—N4. As expected, the remaining bonds in the triazole ring of (1) fall into two sets, the first being the C3—N3 and C5—N3 single bonds, which are longer than the second set of C3—N2 and C5—N1 double bonds. In the most closely related triazole-containing structure in the literature, a similar pattern is observed (van Koningsbruggen *et al.*, 1993). Likewise, the C13—N11 and C12—N10 distances in the acyclic component are intermediate between the values expected for a C—N single bond and a C═N double bond, and are similar to previously reported values [*e.g.* 1.336 (2) Å; Cheng *et al.*, 2006]. The C12—O11 and C13—O12 bonds are between the values expected for a C—O single and a C═O double bond. Thus, there is significant delocalization within the amide bonds of the acyclic component, (2). All other dimensions are within expected ranges.

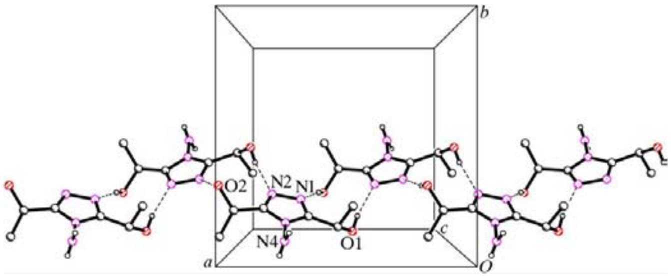

Figure 2

One hydrogen-bonded zigzag chain of triazoles molecules (1). H atoms attached to C atoms have been omitted for clarity. Dashed lines represent hydrogen bonds. Due to symmetry, zigzag chains also run at right angles to this (not shown).

The crystal packing of the 1:1 adduct is stabilized by eight hydrogen bonds, namely four N—H···O, two O—H···N and two O—H···O (Table 2). Two O—H···N bonds between hydroxy atoms O1 and O2 of one triazole and atoms N1 and N2 of two neighbouring triazoles (entries 3 and 4 in Table 2) lead to the formation of approximately linear infinite zigzag chains (Fig. 2; note that, due to symmetry, the zigzag chains also run at right angles to this, approximately along *b*). With two of the four N—H···O bonds, every triazole (1) binds to two acyclic hydrazine (2) molecules (entries 1 and 2 in Table 2). These are the weakest (longest) hydrogen-bond interactions observed in this structure. One hydrazine molecule bridges two triazoles *via* the other two N—H···O bonds (entries 6 and 7 in Table 2). The two O—H···O bonds are the strongest (shortest) hydrogen bonds observed in this structure. These occur between the hydroxy H atoms on atoms O10 and O13 and carbonyl atoms O11 and O12 of two neighbouring hydrazine molecules, respectively (entries 5 and 8 in Table 2), to complete the observed three-dimensional molecular framework.

Experimental

The preparation of (I) follows a slightly modified version of a literature procedure (see *Comment*). Caution! Whilst no problems were encountered in the course of this work, hydrazine and hydrazides are potentially explosive and should therefore be handled with appropriate care. The use of a pure enantiomer of lactic acid, rather than the racemate, was necessary, as the latter always resulted in an oily mixture from which the desired product could not be separated.

Hydrazine hydrate (50 g, 49 ml, 1 mol) was cooled in an ice bath. *S*-Lactic acid (53 g, 0.5 mol, 85% solution in water) was added dropwise with stirring, followed by heating to 373 K overnight. The flask was then equipped for downward distillation and the thermostat temperature was adjusted so as to increase slowly the internal temperature of the flask to 433 K over approximately 3 h (the mixture boils at *ca* 393 K). The flask was then maintained at 433 K overnight. Upon cooling to room temperature, the resulting straw-coloured oil solidified. The oily solid was dissolved in boiling MeCN (1.5 l). The solution was left to cool, producing a large quantity of white crystalline material, which was washed twice with MeCN (20 ml) and dried under reduced pressure to give a 1:1 mixture of (*S*,*S*)-4-amino-3,5-bis(1-hydroxyethyl)-1,2,4-triazole, (1), and (*S*,*S*)-1,2-bis(2-hydroxypropionyl)hydrazine, (2). Attempts to obtain a second crop by reducing the volume of the filtrate were unsuccessful, with any additional product oiling out. Use of a greater excess of hydrazine hydrate, longer reaction times or higher temperatures (Caution!) did not convert the open-chain intermediate, (2), into the desired triazole derivative, (1) (yield 17.3 g, 40%). Analysis: a 1:1 mixture of $C_6H_{12}N_4O_2$ and $C_6H_{12}N_2O_4$ requires: C 41.37, H 6.94, N 24.12%; found: C 41.65, H 6.96, N 24.42%. Suitable single crystals of (I) were grown from a hot dilute acetonitrile solution upon slow cooling overnight. Spectroscopic data are available in the archived CIF.

Crystal data

$C_6H_{12}N_4O_2 \cdot C_6H_{12}N_2O_4$
$M_r = 348.37$
Tetragonal, $P4_32_12$
$a = 9.92960\ (10)$ Å
$c = 34.0538\ (6)$ Å
$V = 3357.60\ (8)$ Å^3
$Z = 8$
$D_x = 1.378$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 150\ (2)$ K
Fragment, colourless
0.45 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.69$, $T_{\max} = 1.00$
18817 measured reflections
3205 independent reflections
3084 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 25.8°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.082$
$S = 1.08$
3205 reflections
245 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 1.2424P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.312 (2)	N3—N4	1.404 (2)
N1—N2	1.409 (2)	C12—N10	1.326 (2)
N2—C3	1.311 (2)	N10—N11	1.391 (2)
C3—N3	1.363 (2)	N11—C13	1.337 (2)
C5—N5	1.363 (2)		
N1—C5—C6—C7	87.7 (2)	C10—C11—C12—N10	110.32 (18)
N2—C3—C8—C9	96.0 (2)	C12—N10—N11—C13	−91.7 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4X···O12$^{\rm i}$	0.92 (3)	2.07 (3)	2.937 (2)	158 (2)
N4—H4Y···O11$^{\rm ii}$	0.72 (3)	2.46 (3)	3.172 (2)	170 (3)
O1—H1X···N2$^{\rm iii}$	0.84 (2)	1.98 (2)	2.808 (2)	170 (2)
O2—H2X···N1$^{\rm iv}$	0.89 (2)	1.94 (2)	2.8056 (19)	165 (2)
O10—H10X···O12$^{\rm v}$	0.91 (2)	1.87 (2)	2.7740 (18)	177 (2)
N10—H10Y···O2$^{\rm iii}$	0.88 (2)	2.02 (2)	2.833 (2)	152.4 (19)
N11—H11X···O1	0.88 (2)	2.04 (2)	2.810 (2)	146.2 (19)
O13—H13X···O11$^{\rm ii}$	0.82 (3)	1.93 (3)	2.7532 (19)	175 (2)

Symmetry codes: (i) $-y+\frac{3}{2}, x+\frac{1}{2}, z-\frac{1}{4}$; (ii) $x-\frac{1}{2}, -y+\frac{5}{2}, -z+\frac{1}{4}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{1}{4}$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{1}{4}$; (v) $-y+2, -x+1, -z+\frac{1}{2}$.

In the absence of significant anomalous scattering, the values of the Flack (1983) parameter were indeterminate (Flack & Bernardinelli, 2000). The synthesis started from pure *S*-lactic acid. All C-bound H atoms were placed in calculated positions, with C—H = 0.98–1.00 Å, and treated as riding on their attached parent atom, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The methyl H atoms were additionally allowed to rotate about the parent C—C bonds. All N- and O-bound H atoms were located in a difference map and their positions were freely refined, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N,O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART* and *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *enCIFer* (Version 1.2; Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3025). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Alonso, J. M., Martin, M. R., de Mendoza, J. & Torres, T. (1987). *Heterocycles*, **26**, 989–1003.
Beckmann, U. & Brooker, S. (2003). *Coord. Chem. Rev.* **245**, 17–29.
Beckmann, U., Brooker, S., Depree, C. V., Ewing, J. D., Moubaraki, B. & Murray, K. (2003). *J. Chem. Soc. Dalton Trans.* pp. 1308–1313.
Beckmann, U., Ewing, J. D. & Brooker, S. (2003). *Chem. Commun.* pp. 1690–1691.
Brandt, C. D., Kitchen, J. A., Beckmann, U., White, N. G., Jameson, G. B. & Brooker, S. (2006). *Supramol. Chem.* In the press.
Bruker (2000). *SMART*, *SAINT* and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
Cheng, C., Sun, J., Wang, C., Zhang, Y., Wei, S., Jiang, F. & Wu, Y. (2006). *Chem. Commun.* pp. 215–217.
Collin, R. L. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 10–14.
Depree, C. V., Beckmann, U., Heslop, K. & Brooker, S. (2003). *J. Chem. Soc. Dalton Trans.* pp. 3071–3081.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Haasnoot, J. G. (2000). *Coord. Chem. Rev.* **200–202**, 131–185.
Kahn, O. (1999). *Chem. Br.* pp. 24–27.
Klingele, M. H., Moubaraki, B., Cashion, J. D., Murray, K. S. & Brooker, S. (2005). *Chem. Commun.* pp. 987–989.
Koningsbruggen, P. J. van, van Hal, J. W., de Graaff, R. A. G., Haasnoot, J. G. & Reedijk, J. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2163–2167.
Liminga, R. (1967). *Acta Chem. Scand.* **21**, 1206–1216.
Liminga, R. & Sorenson, A. M. (1967). *Acta Chem. Scand.* **21**, 2669–2678.
Mendoza, J. de, Ontoria, J. M., Ortega, M. C. & Torres, T. (1992). *Synthesis*, pp. 398–402.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Toda, F., Hyoda, S., Okada, K. & Hirotsu, K. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1531–1532.