Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

[N,N'-Bis(3-aminopropyl)ethylenediamine-κ^4N,N',N'',N'''](trithiocyanurato-κ^2N,S)zinc(II) ethanol solvate

Jaromír Marek,[a]* Pavel Kopel[b] and Zdeněk Trávníček[b,c]

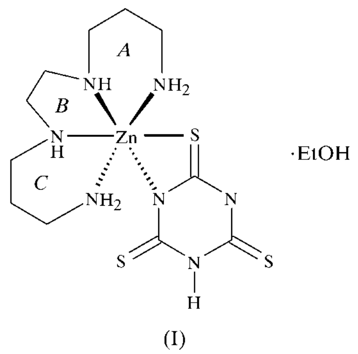
[a]Laboratory of Functional Genomics and Proteomics, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic, [b]Department of Inorganic Chemistry, Faculty of Science, Palacký University, Křížkovského 10, CZ-771 47 Olomouc, Czech Republic, and [c]Laboratory of Growth Regulators, Institute of Experimental Botany, Academy of Science, Šlechtitelů 11, CZ-783 71 Olomouc, Czech Republic
Correspondence e-mail: marek@chemi.muni.cz

Received 15 October 2003
Accepted 7 November 2003
Online 30 November 2003

In the crystal structure of the title compound, [N,N'-bis(3-aminopropyl)ethylenediamine-κ^4N,N',N'',N'''][1,3,5-triazine-2,4,6(1H,3H,5H)-trithionato(2−)-κ^2N,S]zinc(II) ethanol solvate, $[Zn(C_8H_{22}N_4)_2(C_3HN_3S_3)]\cdot C_2H_6O$, the Zn^{II} atom is octahedrally coordinated by four N atoms [Zn—N = 2.104 (2)–2.203 (2) Å] of a tetradentate N-donor N,N'-bis(3-aminopropyl)ethylenediamine (bapen) ligand and by two S and N atoms [Zn—S = 2.5700 (7) Å and Zn—N = 2.313 (2) Å] of a trithiocyanurate(2−) ($ttcH^{2-}$) dianion bonded as a bidentate ligand in a *cis* configuration. The crystal structure of the compound is stabilized by a network of hydrogen bonds.

Comment

Trithiocyanuric acid (2,4,6-trimercaptotriazine, $ttcH_3$) and its trisodium salt have a wide range of applications, *e.g.* they can be used as precipitating agents for heavy metals (Henke *et al.*, 2000; Matlock *et al.*, 2001, 2002). The acid also shows anti-toxoplasmal activity and is more effective than the presently used drugs 5-fluorouracil and emimicin (Iltzsch & Tankersley, 1994). The formation of metal complexes with trithiocyanuric acid depends strongly on pH. At pH values below 5, only $ttcH_3$ exists, which is insoluble in water, while $ttcH_2^-$, $ttcH^{2-}$ and ttc^{3-} anions are formed if the pH is increased. In connection with the extent of $ttcH_3$ deprotonation, the manner of the coordination of the anion to the metal centre can be different and transition metal complexes with various nuclearities can be formed. These complexes can be mononuclear (Mahon *et al.*, 2003; Zhao *et al.*, 2000; Kopel *et al.*, 1998, 2001, 2003; Kopel, Trávníček, Panchártková *et al.*, 1999; Kopel, Trávníček, Kvítek *et al.*, 1999), binuclear (Yamanari *et al.*, 1993), trinuclear (Ainscough *et al.*, 1993; Hunks *et al.*, 1999; Haiduc *et al.*, 2001; Cecconi *et al.*, 2002) or even polynuclear (Chan *et al.*, 1996; Tzeng *et al.*, 1997; Aoki, Shiro & Kimura, 2002; Aoki, Zulkefeli *et al.*, 2002). We report here the preparation and crystal structure of the title mononuclear [Zn(bapen)(ttcH)]·EtOH complex, (I) [bapen is N,N'-bis(3-aminopropyl)ethylenediamine].



(I)

The structure of the title Zn^{II} complex, (I), is very similar to that previously reported for $[Ni(bapen)(ttcH)]\cdot 2H_2O$, (II) (Kopel, Trávníček, Kvítek *et al.*, 1999). Complex (II) is octahedral, with Ni—N(bapen) bond lengths in the range 2.08–2.12 Å, while the Ni—N and Ni—S ($ttcH^{2-}$) distances are 2.143 and 2.521 Å, respectively. These interatomic parameters differ significantly from those found for (I) (Table 1). It is necessary to emphasize that the structure of (I) represents the first known example of a mononuclear Zn^{II} complex with a coordinated trithiocyanurate dianion. If we compare (I) with known Zn^{II}–trithiocyanurate clusters (Aoki, Shiro & Kimura, 2002; Aoki, Zulkefeli *et al.*, 2002), we note that the higher nuclearity of the latter complexes was caused by the total deprotonation of $ttcH_3$, as well as by the use of suitable bridging ligands. To prevent the formation of a polynuclear complex, we have used the bapen ligand for the synthesis of (I).

The crystal structure of (I) consists of [Zn(bapen)(ttcH)] and ethanol molecules (Fig. 1). The Zn^{II} ion in the complex adopts a substantially distorted octahedral geometry, defined by the four N atoms of the bapen ligand and two S and N atoms of the $ttcH^{2-}$ anion in a *cis* configuration. The bapen ligand is bonded as a tetradentate N-donor ligand and forms a five-membered (ring *B*) and two six-membered rings (ring *A*, containing atoms N1 and N2, and ring *C*, containing atoms N4 and N3) with the Zn atom. The Zn—N distances in these rings (2.10–2.20 Å) are comparable with the average length (2.16 Å) of this bond in related complexes in the Cambridge Structural Database (Version 5.24.3; Allen, 2002). The five-membered ring *B* is twisted and both six-membered rings *A* and *C* are in chair conformations. The Cremer–Pople puckering parameters (Cremer & Pople, 1975) are $Q = 0.563$ (3) Å, $\theta = 161.5$ (2)° and $\varphi_2 = -18.8$ (8)° for ring *A*, $Q = 0.575$ (3) Å, $\theta = 165.1$ (2)° and $\varphi_2 = -5.7$ (9)° for ring *C*, and $q_2 = 0.458$ (2) Å and $\varphi_2 = -64.8$ (3)° for ring *B*.

The coordination of the $ttcH^{2-}$ anion to Zn in (I) differs significantly from that in the recently reported polynuclear

DOI: 10.1107/S0108270103025836

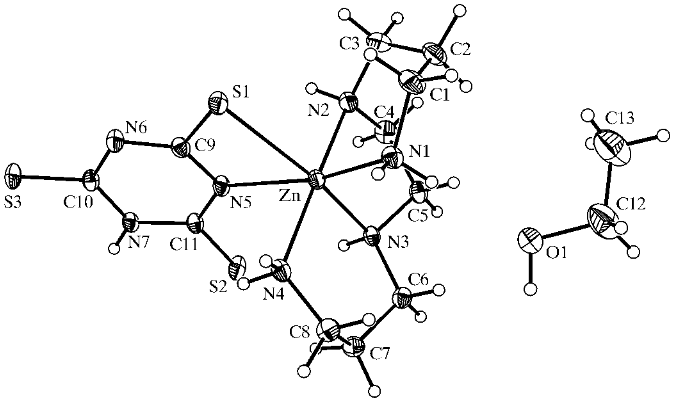


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Zn^{II}–trithiocyanurate structure (Aoki, Zulkefeli *et al.*, 2002). While two distinct average values for the Zn—S (2.30 and 2.88 Å) and Zn—N (3.06 and 2.07 Å) bond distances for two different Zn–ttc coordination modes in Aoki's structure show coordination of the ttc through either S or N atoms, the intermediate values of the Zn—S (2.570 Å) and Zn—N (2.313 Å) bond distances in (I) indicate that $ttcH^{2-}$ is chelated as a bidentate ligand.

In the crystal lattice of (I), Zn complex molecules and molecules of ethanol are linked by a network of hydrogen bonds (Table 2). The shortest such bond (N—H···N = 2.09 Å) connects atoms N4 and N6^{i} of inversion-related molecules [symmetry code: (i) $1 - x, -y, 1 - z$].

Experimental

N,*N*′-Bis(3-aminopropyl)ethylenediamine (0.18 ml, 1 mmol) was added to an ethanol solution (80 ml) of zinc acetate dihydrate (0.22 g, 1 mmol) with stirring at room temperature. Into this solution, the trisodium salt of trithiocyanuric acid nonahydrate ($ttcNa_3 \cdot 9H_2O$; 0.4 g, 1 mmol), dissolved in water (5 ml), was added with stirring over a period of 30 min. The colour of the solution changed to light yellow and a small amount of white precipitate formed. The precipitate was filtered off and discarded, and the filtrate was left to crystallize at room temperature. Light-yellow crystals of (I) were obtained after a week. These were filtered off, washed with a small amount of ethanol and dried in air. Elemental analysis (EA1108 CHNS Analyzer, Fisons Instruments, Beverly, Massachusetts, USA) found: C 33.3, H 6.1, N 21.2, S 21.0%; calculated: C 33.9, H 6.3, N 21.3, S 20.9%.

Crystal data

$[Zn(C_8H_{22}N_4)_2(C_3HN_3S_3)] \cdot C_2H_6O$
$M_r = 460.98$
Triclinic, $P\overline{1}$
$a = 9.0791$ (14) Å
$b = 11.0455$ (15) Å
$c = 11.3580$ (11) Å
$\alpha = 93.592$ (10)°
$\beta = 102.316$ (11)°
$\gamma = 112.167$ (14)°
$V = 1017.6$ (3) Å^3
$Z = 2$
$D_x = 1.505$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2410 reflections
$\theta = 26.5$–2.2°
$\mu = 1.53$ mm^{-1}
$T = 120$ (2) K
Prism, light yellow
0.40 × 0.40 × 0.40 mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Rotation method, ω scans
6681 measured reflections
4458 independent reflections
4279 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.4°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 14$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.01$
4458 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 1.75P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N1	2.104 (2)	Zn—S1	2.5700 (7)
Zn—N4	2.1249 (19)	S1—C9	1.708 (2)
Zn—N3	2.1682 (19)	S2—C11	1.697 (2)
Zn—N2	2.2031 (19)	S3—C10	1.698 (2)
Zn—N5	2.3132 (18)		
N1—Zn—N4	94.66 (8)	N2—Zn—S1	89.91 (6)
N1—Zn—N3	100.92 (7)	N5—Zn—S1	64.32 (5)
N4—Zn—N3	90.46 (7)	C9—S1—Zn	80.99 (8)
N1—Zn—N2	93.77 (8)	C1—N1—Zn	116.11 (15)
N4—Zn—N2	169.06 (8)	N6—C9—N5	124.5 (2)
N3—Zn—N2	81.09 (7)	N6—C9—S1	120.12 (16)
N1—Zn—N5	163.89 (7)	N5—C9—S1	115.42 (16)
N4—Zn—N5	84.67 (7)	N6—C10—N7	119.33 (19)
N3—Zn—N5	95.18 (7)	N6—C10—S3	121.87 (17)
N2—Zn—N5	89.15 (7)	N7—C10—S3	118.77 (17)
N1—Zn—S1	99.81 (6)	N5—C11—N7	117.62 (19)
N4—Zn—S1	95.51 (5)	N5—C11—S2	122.90 (17)
N3—Zn—S1	157.87 (5)	N7—C11—S2	119.48 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O1	0.92	2.20	3.065 (3)	156
N1—H1*A*···S3^{i}	0.92	2.55	3.458 (2)	167
N3—H3···S2	0.93	2.61	3.475 (2)	154
N4—H4*A*···N6^{i}	0.92	2.09	2.991 (3)	167
N7—H7···S2^{ii}	0.88	2.49	3.361 (2)	170
O1—H1O···S3^{iii}	0.93 (4)	2.46 (4)	3.357 (2)	161 (3)
O1—H1O···N6^{iii}	0.93 (4)	2.61 (3)	3.326 (3)	135 (3)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $x, y, 1 + z$.

H atoms attached to C and N atoms were positioned geometrically, with C—H distances of 0.99 Å and N—H distances in the range 0.88–0.93 Å, and with U_{iso}(H) values derived from the U_{eq} values of the corresponding C or N atoms. The parameters of atom H1O attached to atom O1 were refined, with the O···H distance restrained to 0.95 (2) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97

(Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

The financial support of this work by the Ministry of Education of the Czech Republic (MŠMT) (grant Nos. 143100008 and 153100008) and the Grant Agency of the Czech Republic (GAČR) (grant No. 203/02/0436) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1284). Services for accessing these data are described at the back of the journal.

References

Ainscough, E. W., Brodie, A. M., Collect, R. K., Mair, A. J. A. & Waters, J. M. (1993). *Inorg. Chim. Acta*, **214**, 21–22.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Aoki, S., Shiro, M. & Kimura, E. (2002). *Chem. Eur. J.* **8**, 929–939.

Aoki, S., Zulkefeli, M., Shiro, M. & Kimura, E. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4894–4896.

Cecconi, F., Ghilardi, C. A., Midollini, S. & Orlandini, A. (2002). *J. Organomet. Chem.* **645**, 101–104.

Chan, C. K., Cheung, K. K. & Che, C. M. (1996). *J. Chem. Soc. Chem. Commun.* pp. 227–228.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Haiduc, I., Mahon, M. F., Molloy, K. C. & Venter, M. M. (2001). *J. Organomet. Chem.* **627**, 6–12.

Henke, K. R., Robertson, D., Krepps, M. K. & Atwood, D. A. (2000). *Water Res.* **34**, 3005–3013.

Hunks, W. J., Jennings, M. C. & Puddephatt, R. J. (1999). *Inorg. Chem.* **38**, 5930–5931.

Iltzsch, M. H. & Tankersley, K. O. (1994). *Biochem. Pharmacol.* **48**, 781–792.

Johnson, C. K. & Burnett, M. N. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Kopel, P., Trávníček, Z., Kvítek, L., Biler, M., Pavlíček, M., Šindelář, Z. & Marek, J. (2001). *Transition Met. Chem.* **26**, 282–286.

Kopel, P., Trávníček, Z., Kvítek, L., Černošek, Z., Wrzeszcz, G. & Marek, J. (2003). *J. Coord. Chem.* **56**, 1–11.

Kopel, P., Trávníček, Z., Kvítek, L., Panchártková, R., Biler, M., Marek, J. & Nádvorník, M. (1999). *Polyhedron*, **18**, 1779–1784.

Kopel, P., Trávníček, Z., Panchártková, R., Biler, M. & Marek, J. (1999). *Transition Met. Chem.* **24**, 239–243.

Kopel, P., Trávníček, Z., Panchártková, R., Šindelář, Z. & Marek, J. (1998). *J. Coord. Chem.* **44**, 205–215.

Mahon, M. F., Molloy, K. C., Venter, M. M. & Haiduc, I. (2003). *Inorg. Chim. Acta*, **348**, 75–81.

Matlock, M. M., Henke, K. R. & Atwood, D. A. (2002). *J. Hazard. Mater. B*, **92**, 129–142.

Matlock, M. M., Henke, K. R., Atwood, D. A. & Robertson, D. (2001). *Water Res.* **35**, 3649–3655.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Oxford Diffraction (2002). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.69. Oxford Diffraction Ltd, Abingdon, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Tzeng, B. C., Che, C. M. & Peng, S. M. (1997). *J. Chem. Soc. Chem. Commun.* pp. 1771–1772.

Yamanari, K., Kushi, Y., Yamamoto, M., Fuyuhiro, A., Kaizaki, S., Kawamoto, T. & Kushi, Y. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3715–3721.

Zhao, Y., Su, W., Cao, R. & Hong, M. (2000). *Acta Cryst.* C**56**, e331–e333.