

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A* **24**, 351–359.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

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Bis(antazoline)dichlorozinc(II)

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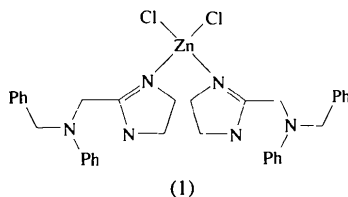
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Abstract

The structure of the title compound, dichlorobis-[4,5-dihydro-*N*-phenyl-*N*-(phenylmethyl)-1*H*-imidazole-2-methanamine-*N*³]zinc(II), [ZnCl₂(C₁₇H₁₉N₃)₂], is composed of discrete molecules wherein zinc is coordinated to two molecules of antazoline, *via* imidazole N atoms, and two Cl atoms. The geometry around the Zn atom is slightly distorted tetrahedral, with Zn—N bond distances of 2.039 (8) and 2.004 (9) Å, Zn—Cl bond distances of 2.243 (3) and 2.259 (3) Å, and Cl—Zn—Cl and N—Zn—N angles of 116.3 (1) and 108.4 (4)°, respectively.

Comment

Continuing our interest in the studies of anti-allergic drugs effective on H1-type receptor sites, we have synthesized the title compound, (1), which is a transition metal complex of the anti-allergic drug antazoline. In this paper we report the crystal structure of (1), which has been determined in an attempt to understand the influence of transition metals on the conformation of anti-allergic drugs.



An *ORTEPII* drawing (Johnson, 1976) of the title compound is presented in Fig. 1 together with the atomic numbering scheme. In the crystal structure of (1), the Zn atom has slightly distorted tetrahedral geometry with Zn—Cl bond distances of

2.243 (3) and 2.259 (3) Å, and Zn—N distances of 2.039 (8) and 2.004 (9) Å, which are in accord with the corresponding distances reported for the crystal structures of dichlorobis(xanthine)zinc(II) [Zn—Cl 2.240 (1) and Zn—N 2.029 (3) Å; Dubler, Hanggi & Schmale, 1992], dichlorobis(imidazole)zinc(II) [Zn—Cl 2.258 (3) and 2.239 (3) Å, and Zn—N 1.995 (11) and 2.020 (11) Å; Lundberg, 1966], dichlorobis{[3-(imidazol-1-yl)-1-oxopropyl]benzene-*N*}zinc(II) [Zn—Cl 2.226 (1) and 2.242 (1) Å, and Zn—N 2.029 (2) and 2.013 (3) Å; Bremer, Uhlenbrock, Pinkerton & Krebs, 1993] and dichlorobis(1,2-dimethylimidazole)zinc(II) [Zn—Cl 2.2509 (8) and 2.2468 (8) Å, and Zn—N 2.006 (3) and 2.008 (3) Å; Bharadwaj, Schugar & Potenza, 1991].

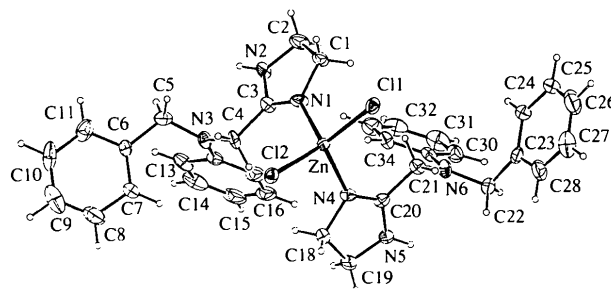


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the title compound showing the numbering scheme. The non-H atoms are plotted as displacement ellipsoids of 30% probability.

The molecular dimensions in the ligated antazoline fragment are unexceptional [mean bond lengths C=N 1.26 (1), C_{sp²}—N 1.36 (1), C_{sp³}—N 1.46 (1) and C—C(aromatic) 1.37 (2) Å] and agree well with the dimensions of antazoline hydrochloride (Bertolasi, Borea & Gilli, 1982). The imidazole ring in antazoline hydrochloride, however, unlike in (1), has delocalized charge with equal C—N distances, which are between single- and double-bond distances.

The most interesting features of the complex are the angles between the least-squares planes. For example, the N3,C4,C5,C12—C17 moiety and its corresponding moiety in the other half of the complex, both of which are essentially planar [mean deviations 0.04 (1) and 0.03 (1) Å, respectively], are inclined at almost right angles with respect to the imidazole rings [92.4 (9) and 84.9 (9)°, respectively]; the corresponding angle in antazoline hydrochloride is 69.3°. The angles between the C6—C11 and C23—C28 phenyl ring planes and their respective imidazole rings in the two antazoline units of the complex are 47.7 (12) and 89.7 (10)°, compared with 85.0° in antazoline hydrochloride. The angles between the mean planes of the phenyl rings within each ligated antazoline moiety of the complex [84.6 (11) and 99.5 (12)°] are somewhat close to the corresponding angle of 102.5° in antazoline hydrochloride.

Experimental

The title compound was synthesized according to the method of Malone, Miskelly & Parvez (1977) by mixing 1.92 mmol of antazoline hydrochloride (Sigma Inc.) with 0.92 mmol of anhydrous zinc chloride in aqueous medium and adding ammonium hydroxide to this solution. The light brown crystals thus obtained were recrystallized from acetonitrile by slow evaporation to yield colourless needles.

Crystal data

[ZnCl₂(C₁₇H₁₉N₃)₂]

$M_r = 667.00$

Triclinic

$a = 8.324(2) \text{ \AA}$

$b = 24.833(5) \text{ \AA}$

$c = 8.178(1) \text{ \AA}$

$\alpha = 95.76(2)^\circ$

$\beta = 90.62(2)^\circ$

$\gamma = 90.87(2)^\circ$

$V = 1681.6(5) \text{ \AA}^3$

$Z = 2$

$D_x = 1.317 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 14.1\text{--}16.3^\circ$

$\mu = 0.922 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Needle

$0.50 \times 0.16 \times 0.09 \text{ mm}$

Colourless

C2	0.7611 (14)	0.2197 (5)	0.3137 (17)	0.077 (5)
C3	0.5943 (13)	0.2870 (4)	0.2523 (15)	0.052 (4)
C4	0.5520 (14)	0.3427 (4)	0.2159 (15)	0.059 (4)
C5	0.7444 (14)	0.4146 (5)	0.3208 (16)	0.069 (5)
C6	0.6897 (14)	0.4724 (4)	0.3251 (15)	0.050 (4)
C7	0.5690 (18)	0.4871 (5)	0.2265 (17)	0.082 (5)
C8	0.525 (2)	0.5421 (7)	0.240 (2)	0.108 (7)
C9	0.592 (3)	0.5788 (7)	0.345 (3)	0.114 (9)
C10	0.710 (2)	0.5635 (7)	0.447 (3)	0.115 (8)
C11	0.7604 (15)	0.5108 (7)	0.4366 (19)	0.091 (6)
C12	0.7569 (14)	0.3746 (5)	0.0285 (17)	0.052 (4)
C13	0.8755 (16)	0.4130 (5)	-0.0044 (19)	0.075 (5)
C14	0.9422 (17)	0.4089 (7)	-0.161 (2)	0.089 (7)
C15	0.895 (3)	0.3711 (8)	-0.278 (2)	0.118 (9)
C16	0.779 (2)	0.3332 (7)	-0.250 (2)	0.104 (8)
C17	0.7094 (16)	0.3362 (6)	-0.094 (2)	0.077 (6)
C18	0.1842 (15)	0.2882 (4)	-0.1096 (16)	0.067 (5)
C19	0.2037 (17)	0.2715 (5)	-0.2930 (15)	0.079 (5)
C20	0.2526 (12)	0.2022 (5)	-0.1453 (17)	0.049 (4)
C21	0.2874 (13)	0.1442 (5)	-0.1137 (15)	0.054 (4)
C22	0.2742 (15)	0.0726 (5)	-0.3485 (16)	0.073 (5)
C23	0.2399 (18)	0.0238 (5)	-0.2600 (14)	0.064 (5)
C24	0.3575 (19)	-0.0044 (6)	-0.1874 (19)	0.098 (6)
C25	0.318 (3)	-0.0503 (7)	-0.114 (2)	0.124 (8)
C26	0.160 (3)	-0.0670 (7)	-0.108 (2)	0.132 (10)
C27	0.044 (2)	-0.0400 (7)	-0.183 (2)	0.109 (8)
C28	0.083 (2)	0.0051 (6)	-0.2549 (18)	0.088 (6)
C29	0.5304 (15)	0.1252 (4)	-0.2738 (15)	0.049 (4)
C30	0.6176 (18)	0.0950 (5)	-0.3951 (17)	0.069 (5)
C31	0.777 (2)	0.1082 (7)	-0.424 (2)	0.099 (7)
C32	0.8544 (18)	0.1506 (8)	-0.330 (2)	0.091 (7)
C33	0.7722 (17)	0.1776 (6)	-0.211 (2)	0.086 (6)
C34	0.6115 (16)	0.1673 (4)	-0.1787 (16)	0.062 (5)

Data collection

Rigaku AFC-6S diffractometer

2265 observed reflections

$[I > 2\sigma(I)]$

$\omega/2\theta$ scans

$R_{\text{int}} = 0.0252$

Absorption correction:

$\theta_{\text{max}} = 25.0^\circ$

ψ scan (North, Phillips & Mathews, 1968)

$h = 0 \rightarrow 9$

$T_{\text{min}} = 0.762$, $T_{\text{max}} = 0.999$

$k = -29 \rightarrow 29$

$l = -9 \rightarrow 9$

3 standard reflections

6389 measured reflections

frequency: 120 min

5941 independent reflections

intensity decay: 0.2%

Refinement

Refinement on F

Weighting scheme based

$R = 0.061$

on measured e.s.d.'s

$wR = 0.059$

$(\Delta/\sigma)_{\text{max}} = 0.008$

$S = 1.99$

$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$

2265 reflections

$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$

388 parameters

Atomic scattering factors

H atoms geometrically

from *International Tables*

idealized (riding with C—

for *X-ray Crystallography*

H and N—H = 0.95 \AA)

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
Zn	0.2580 (2)	0.2423 (1)	0.2151 (2)	0.0410 (4)
Cl1	0.1826 (3)	0.1656 (1)	0.3184 (3)	0.057 (1)
Cl2	0.1233 (3)	0.3176 (1)	0.3060 (4)	0.053 (1)
N1	0.4975 (10)	0.2490 (4)	0.2698 (12)	0.058 (3)
N2	0.7472 (11)	0.2752 (3)	0.2878 (13)	0.068 (4)
N3	0.6867 (11)	0.3774 (3)	0.1810 (14)	0.052 (3)
N4	0.2301 (10)	0.2387 (4)	-0.0295 (11)	0.046 (3)
N5	0.2387 (11)	0.2151 (4)	-0.2978 (12)	0.057 (4)
N6	0.3688 (12)	0.1142 (3)	-0.2466 (12)	0.057 (4)
Cl	0.5870 (14)	0.2038 (4)	0.3266 (16)	0.066 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Zn—Cl1	2.243 (3)	N4—C20	1.26 (1)
Zn—Cl2	2.259 (3)	N5—C19	1.43 (1)
Zn—N1	2.039 (8)	N5—C20	1.32 (1)
Zn—N4	2.004 (9)	N6—C21	1.44 (1)
N1—C1	1.47 (1)	N6—C22	1.47 (1)
N1—C3	1.25 (1)	N6—C29	1.39 (1)
N2—C2	1.42 (1)	C1—C2	1.50 (1)
N2—C3	1.35 (1)	C3—C4	1.49 (1)
N3—C4	1.45 (1)	C5—C6	1.51 (1)
N3—C5	1.47 (1)	C18—C19	1.53 (2)
N3—C12	1.38 (1)	C20—C21	1.52 (1)
N4—C18	1.50 (1)	C22—C23	1.50 (2)
Cl1—Zn—Cl2	116.3 (1)	C21—N6—C22	117.1 (10)
Cl1—Zn—N1	103.6 (3)	C21—N6—C29	119.8 (10)
Cl1—Zn—N4	113.2 (3)	C22—N6—C29	123 (1)
Cl2—Zn—N1	112.4 (3)	N1—C1—C2	105.0 (9)
Cl2—Zn—N4	103.1 (3)	N2—C2—C1	100.7 (9)
N1—Zn—N4	108.4 (4)	N1—C3—N2	113.0 (10)
Zn—N1—C1	121.6 (7)	N1—C3—C4	126 (1)
Zn—N1—C3	129.6 (8)	N2—C3—C4	120.4 (10)
C1—N1—C3	108.6 (9)	N3—C4—C3	115.5 (9)
C2—N2—C3	111.0 (8)	N3—C5—C6	116.2 (10)
C4—N3—C5	115 (1)	N4—C18—C19	104.0 (9)
C4—N3—C12	122 (1)	N5—C19—C18	102.9 (9)
C5—N3—C12	122.8 (10)	N4—C20—N5	117 (1)
Zn—N4—C18	120.4 (7)	N4—C20—C21	121 (1)
Zn—N4—C20	133.5 (9)	N5—C20—C21	120 (1)
C18—N4—C20	105.9 (10)	N6—C21—C20	113.5 (10)
C19—N5—C20	108.7 (9)	N6—C22—C23	112 (1)

The space group was determined from the statistical analysis of intensity distribution and the successful solution and refinement of the structure.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *PATY* in *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We thank the Natural Sciences and Engineering Research Council, Canada, for providing the diffractometer through an equipment grant to the University of Calgary.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: FG1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bertolasi, V., Borea, P. A. & Gilli, G. (1982). *Acta Cryst.* B38, 2522–2525.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.
- Bharadwaj, P. K., Schugar, H. J. & Potenza, J. A. (1991). *Acta Cryst.* C47, 754–757.
- Bremer, J., Uhlenbrock, S., Pinkerton, A. A. & Krebs, B. (1993). *Z. Anorg. Allg. Chem.* 619, 1183–1195.
- Dubler, E., Hanggi, G. & Schmalle, H. (1992). *Inorg. Chem.* 31, 3728–3736.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lundberg, B. K. S. (1966). *Acta Cryst.* 21, 901–909.
- Malone, J. F., Miskelly, M. & Parvez, M. (1977). *Proc. R. Ir. Acad. Sect. B* (RIC Centenary Issue), 77, 499–505.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

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Tetrakis(μ -acetato- $O:O'$)bis(1,5,9-triazacyclododecane-2,4-dione- N^9)dicopper(II)-($Cu-Cu$)

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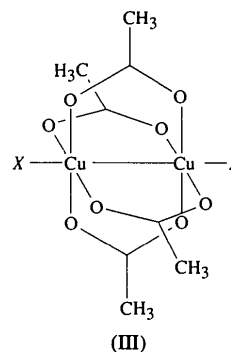
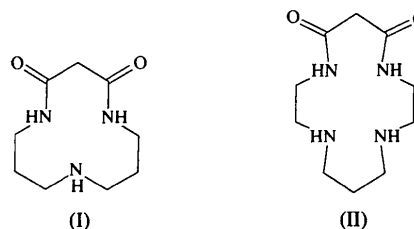
Abstract

The title compound, $[Cu_2(C_2H_3O_2)_4(C_9H_{17}N_3O_2)_2]$, is centrosymmetric and consists of a tetrakis(acetato)-bridged dinuclear copper(II) core with two unidentate N-

donor axial ligands, each coordinated *via* the secondary amine N atom rather than through one of the two amide N atoms. The Cu—Cu distance of 2.702 (3) Å is longer than previously reported for copper(II) acetate dimers of this type. Intermolecular hydrogen bonding occurs between the amide O and N atoms.

Comment

Diamine tetraaza macrocycles such as dioxocyclam, (II), have been shown (Kimura, Koike, Machida, Nagai & Kodama, 1984; Machida, Kimura & Kodama, 1983) to coordinate divalent metal cations (*e.g.* Cu^{2+} , Ni^{2+} and Co^{2+}) within the macrocyclic cavity, with simultaneous loss of the two amide protons and the formation of uncharged square-planar complexes. An objective of this work was to investigate whether the ligand 1,5,9-triazacyclododecane-2,4-dione, (I), would react in an analogous manner. The macrocycle (I) has been used previously as a precursor in the synthesis of several pendent-arm macrocyclic ligands (Helps, Parker, Jankowski, Chapman & Nicholson, 1989; Rawle, Clarke, Moore & Alcock, 1992) but its complexation characteristics have never been investigated.



The reaction of (I) with copper(II) acetate monohydrate produced the title compound (IV), the molecular structure of which is shown in Fig. 1. Clearly, the macrocycle only acts as a monodentate ligand in this complex, and has simply replaced the axial water molecules in the original acetate structure. The coordination is *via* the secondary amine N atom and the amide protons are not dissociated [*i.e.* the reaction is not analogous to those of the ligand (II)].