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Clemizoledichlorozinc(II)

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Abstract

The crystal structure of the title compound, dichloro[1-(p-chlorophenylmethyl)-2-(1-pyrrolidinylmethyl)benz-imidazole-N,N'']zinc(II), [ZnCl$_2$(C$_{19}$H$_{20}$ClN$_3$)], is composed of independent molecules wherein clemizole acts as a bidentate ligand and is coordinated to zinc *via* pyrrolidinyl and imidazole N atoms. The geometry around zinc is distorted tetrahedral with bond distances Zn—N 2.029 (3) and 2.157 (3) Å, and Zn—Cl 2.196 (2) and 2.222 (2) Å.

Comment

The crystal structures of clemizole hydrochloride (Parvez, 1996) and clemizole in its free form (Parvez & Sabir, 1996) have been reported. We have now incorporated this important antihistamine into a transition metal complex to investigate the effects such complex formation may have on the conformation of the drug molecule. In this paper, we report the crystal structure of clemizoledichlorozinc(II), (1).
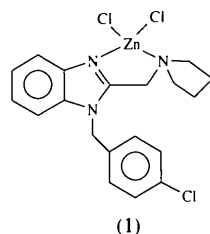
(1)

Fig. 1 shows an *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. The drug molecule acts as a bidentate ligand and is coordinated *via* pyrrolidinyl and imidazole N atoms to zinc with Zn—N distances of 2.029 (3) and

2.157 (3) Å. The Zn atom is also bonded to two Cl atoms with distances of 2.196 (2) and 2.222 (2) Å. The geometry around zinc is distorted tetrahedral. Similar distances and geometries have been reported for a number of closely related zinc complexes, *e.g.* bis(antazoline)-dichlorozinc(II) (Parvez & Rusiewicz, 1995), bis-(xanthine)dichlorozinc(II) (Dubler, Hanggi & Schmalle, 1992), bis(imidazole)dichlorozinc(II) (Lundberg, 1966), bis(1,2-dimethylimidazole)dichlorozinc(II) (Bharadwaj, Schugar & Potenza, 1991), bis{[3-(imidazol-1-yl)-1-oxopropyl]benzene-N}dichlorozinc(II) (Bremer, Uhlenbrock, Pinkerton & Krebs, 1993) and (2,2'-bipyridine)-dichlorozinc(II) (Khan & Tuck, 1984).
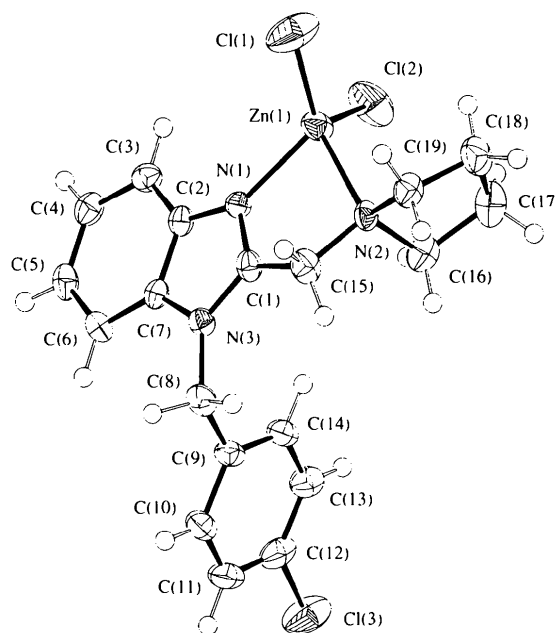

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

The molecular dimensions in the clemizole ligand are normal with bond distances C$_{sp^2}$—Cl 1.748 (5) and C=N 1.321 (5) and mean C$_{sp^3}$—C$_{sp^2}$ 1.505 (7), C$_{sp^3}$—C$_{sp^3}$ 1.525 (8), C—C$_{aromatic}$ 1.386 (8), N—C$_{sp^3}$ 1.476 (7), and N—C$_{sp^2}$(imidazole ring N atoms fused to benzene) 1.394 (4) Å; the N—C$_{sp^2}$ distance C(1)—N(3) [1.357 (5) Å] is significantly shorter than the other two corresponding distances.

The benzimidazole and the phenyl rings are essentially planar with maximum deviations of atoms from the least-squares planes being 0.015 (4) and 0.011 (4) Å, respectively. The dihedral angle between these planes is 81.1 (4)°; the corresponding angles in the crystal structures of clemizole hydrochloride and clemizole free base have been observed to be 82.8 (9) (Parvez, 1996) and 68.8 (6)° (Parvez & Sabir, 1996), respectively. The pyrrolidinyl ring has an N(2)-envelope conformation

with N(2) 0.648 (4) Å out of the plane of the remaining four C atoms of the ring; a similar conformation of the five-membered ring has been observed in the crystal structure of clemizole hydrochloride and clemizole free base, mentioned above.

Experimental

The title compound was synthesized by the method described earlier for dichlorobis(antazoline)zinc(II) (Parvez & Rusiewicz, 1995). Colourless prismatic crystals were obtained from a solution of ethanol by slow evaporation at room temperature.

Crystal data

[ZnCl₂(C₁₉H₂₀ClN₃)]	Mo $K\alpha$ radiation
$M_r = 462.13$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 12.365 (3)$ Å	$\theta = 10–15°$
$b = 13.192 (3)$ Å	$\mu = 1.635$ mm^{-1}
$c = 13.373 (2)$ Å	$T = 170$ K
$\beta = 113.38 (2)°$	Prism
$V = 2002.3 (8)$ Å³	$0.48 \times 0.22 \times 0.20$ mm
$Z = 4$	Colourless
$D_x = 1.533$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-6S diffractometer	1925 observed reflections
$\omega/2\theta$ scans	$[I > 3\sigma(I)]$]
Absorption correction:	$R_{int} = 0.0384$
ψ scan (North, Phillips & Mathews, 1968)	$\theta_{max} = 25°$
$T_{min} = 0.925$, $T_{max} = 1.000$	$h = 0 \to 14$
	$k = 0 \to 15$
	$l = -15 \to 14$
3898 measured reflections	3 standard reflections
3719 independent reflections	monitored every 200 reflections
	intensity decay: 0.29%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.0063$
$R = 0.033$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
$wR = 0.031$	$\Delta\rho_{min} = -0.26$ e Å^{-3}
$S = 1.273$	Extinction correction: none
1925 reflections	Atomic scattering factors
235 parameters	from International Tables
H atoms riding with C—H 0.95 Å	for X-ray Crystallography (1974, Vol. IV)
$w = 1/[\sigma^2(F_o) + 0.018(F_o^2)]$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Zn(1)	0.57032 (5)	0.22647 (4)	0.11796 (5)	0.0330 (1)
Cl(1)	0.4228 (1)	0.1299 (1)	0.0166 (1)	0.0725 (5)
Cl(2)	0.5364 (1)	0.3677 (1)	0.1914 (1)	0.0626 (5)
Cl(3)	1.3463 (1)	0.4869 (1)	0.4352 (1)	0.0631 (5)
N(1)	0.6993 (3)	0.2568 (3)	0.0645 (3)	0.025 (1)
N(2)	0.7061 (3)	0.1309 (3)	0.2299 (3)	0.026 (1)
N(3)	0.8840 (3)	0.2284 (3)	0.0855 (3)	0.025 (1)
C(1)	0.7929 (4)	0.1987 (3)	0.1108 (3)	0.027 (1)
C(2)	0.7298 (4)	0.3297 (3)	0.0054 (3)	0.025 (1)
C(3)	0.6649 (4)	0.4095 (3)	-0.0593 (4)	0.029 (1)
C(4)	0.7192 (4)	0.4683 (3)	-0.1112 (3)	0.033 (1)
C(5)	0.8347 (4)	0.4488 (3)	-0.0993 (4)	0.033 (1)
C(6)	0.9007 (4)	0.3709 (3)	-0.0346 (3)	0.029 (1)
C(7)	0.8451 (4)	0.3119 (3)	0.0160 (3)	0.024 (1)
C(8)	1.0054 (4)	0.1901 (3)	0.1295 (4)	0.033 (1)
C(9)	1.0901 (3)	0.2642 (3)	0.2082 (3)	0.028 (1)
C(10)	1.2058 (4)	0.2673 (4)	0.2156 (4)	0.036 (1)
C(11)	1.2851 (4)	0.3350 (4)	0.2875 (4)	0.042 (2)
C(12)	1.2482 (4)	0.3985 (4)	0.3488 (4)	0.040 (2)
C(13)	1.1344 (4)	0.3956 (3)	0.3431 (4)	0.037 (1)
C(14)	1.0563 (4)	0.3269 (3)	0.2729 (4)	0.032 (1)
C(15)	0.7882 (4)	0.1089 (3)	0.1775 (4)	0.035 (1)
C(16)	0.7643 (4)	0.1851 (4)	0.3353 (4)	0.040 (2)
C(17)	0.6817 (5)	0.1684 (4)	0.3935 (4)	0.052 (2)
C(18)	0.6047 (4)	0.0778 (4)	0.3351 (4)	0.046 (2)
C(19)	0.6612 (4)	0.0378 (3)	0.2612 (4)	0.034 (1)

Table 2. *Selected geometric parameters* (Å, °)

Zn(1)—Cl(1)	2.196 (2)	N(2)—C(19)	1.476 (5)
Zn(1)—Cl(2)	2.222 (2)	N(3)—C(1)	1.357 (5)
Zn(1)—N(1)	2.029 (3)	N(3)—C(7)	1.398 (5)
Zn(1)—N(2)	2.157 (3)	N(3)—C(8)	1.467 (5)
Cl(3)—C(12)	1.748 (5)	C(1)—C(15)	1.497 (6)
N(1)—C(1)	1.321 (5)	C(8)—C(9)	1.512 (6)
N(1)—C(2)	1.390 (5)	C(16)—C(17)	1.527 (7)
N(2)—C(15)	1.474 (5)	C(17)—C(18)	1.534 (7)
N(2)—C(16)	1.487 (5)	C(18)—C(19)	1.514 (6)
Cl(1)—Zn(1)—Cl(2)	120.18 (6)	C(1)—N(3)—C(8)	128.3 (4)
Cl(1)—Zn(1)—N(1)	118.3 (1)	C(7)—N(3)—C(8)	124.5 (3)
Cl(1)—Zn(1)—N(2)	108.4 (1)	N(1)—C(1)—N(3)	112.1 (4)
Cl(2)—Zn(1)—N(1)	107.6 (1)	N(1)—C(1)—C(15)	120.3 (4)
Cl(2)—Zn(1)—N(2)	114.5 (1)	N(3)—C(1)—C(15)	127.6 (4)
N(1)—Zn(1)—N(2)	81.7 (1)	N(1)—C(2)—C(3)	130.9 (4)
Zn(1)—N(1)—C(1)	112.7 (3)	N(1)—C(2)—C(7)	108.8 (4)
Zn(1)—N(1)—C(2)	140.0 (3)	N(3)—C(7)—C(2)	105.7 (4)
C(1)—N(1)—C(2)	106.5 (3)	N(3)—C(7)—C(6)	131.5 (4)
Zn(1)—N(2)—C(15)	106.2 (2)	N(3)—C(8)—C(9)	111.9 (3)
Zn(1)—N(2)—C(16)	109.1 (3)	N(2)—C(15)—C(1)	108.9 (3)
Zn(1)—N(2)—C(19)	114.0 (3)	N(2)—C(16)—C(17)	104.1 (4)
C(15)—N(2)—C(16)	112.3 (3)	C(16)—C(17)—C(18)	105.0 (4)
C(15)—N(2)—C(19)	112.3 (3)	C(17)—C(18)—C(19)	104.5 (4)
C(16)—N(2)—C(19)	103.1 (3)	N(2)—C(19)—C(18)	102.6 (4)
C(1)—N(3)—C(7)	107.0 (3)		

The space group, $P2_1/n$, was determined uniquely from the systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$.

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: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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(Dicyanamido)bis(1,10-phenanthroline)-copper(II) Tricyanomethanide

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Abstract

The crystal structure of $[Cu(C_{12}H_8N_2)_2\{N(CN)_2\}]$-$[C(CN)_3]$ is formed by discrete $[Cu(phen)_2\{N(CN)_2\}]^+$ cations and $[C(CN)_3]^-$ anions (phen = 1,10-phenanthroline). The coordination polyhedron of Cu^{II} is a distorted trigonal bipyramid with a CuN_5 chromophore.

Comment

Crystal structures of five-coordinate copper compounds with the general formula $[Cu(phen)_2X_2]$, where X = NCS and NCSe, are known (Sedov, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1982). The pseudo-halide ligands are in a *cis* configuration in an equatorial plane and the
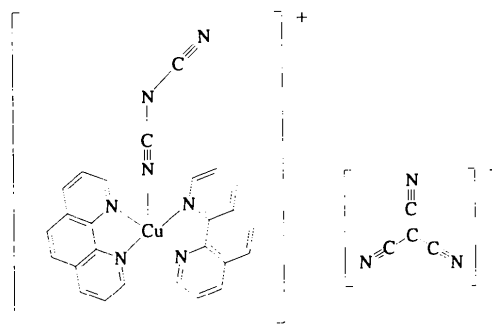
two phen molecules occupy both equatorial and axial positions. Recently, we have published the structure of a complex with the same general formula, with X = $N(CN)_2$. The two dicyanamide ligands are also in a *cis* configuration but one occupies the axial while the second one the equatorial plane. One phen molecule occupies both the equatorial and the axial position, as in the previous cases, but the second phen molecule is coordinated only in the equatorial plane (Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995). We have also published structures of two five-coordinate $[Cu(phen)_2X][C(CN)_3].nH_2O$ complexes, with X = NCS, n = 0 and X = CN, n = 2 (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996a,b). The phenanthroline molecules occupy both the equatorial and the axial positions, as in the six-coordinate compounds with X = NCS and NCSe. We decided to prepare a five-coordinate compound with X = $N(CN)_2$ to find out whether the coordination polyhedron around the Cu^{II} atom will be of the same type as in previous five-coordinate complexes or whether dicyanamide will induce differences in the coordination polyhedron similar to those of the six-coordinate complex $[Cu(phen)_2\{N(CN)_{22}\}]$.

Fig. 1 shows the labelling scheme of one formula unit. The Cu atom is fivefold coordinated by two phen molecules and by one $N(CN)_2^-$ ligand (in the equatorial plane). The coordination polyhedron is a distorted trigonal bipyramid. The tcm⁻ anion $\{[C(CN)_3]^-\}$ does not enter the inner coordination sphere. In the trigonal bipyramid the two out-of-plane Cu—N11 and Cu—N31 distances are practically of the same length [1.977 (4) and 1.981 (3) Å, respectively] and are almost collinear [N11—Cu—N31 = 175.12 (14)°]. The two in-plane distances (Cu—N21 and Cu—N41) also have similar values [2.064 (3) and 2.112 (4) Å, respectively], but they are longer on average than the out-of-plane Cu—N distances by 0.109 Å. The third in-plane Cu—N2 distance of 1.982 (4) Å is significantly shorter than the other two. The out-of-plane angles lie within the range 80.7–95.2°. The same features of the coordination polyhedron as well as similar values of the appropriate bond distances and angles were observed in the structures of both above five-coordinate Cu complexes with the same tcm⁻ counteranion.