metal-organic compounds

Trichloro(1,1-dimethylbiguanidium-κN^3)zinc(II)

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The title compound, [ZnCl$_3$(C$_4$H$_{12}$N$_5$)], was prepared from aqueous solution and its structure determined. The coordination geometry around the Zn atom is a tetrahedron, with the central Zn atom bound to three Cl atoms and to one N atom of the biguanide ligand. The dihedral angle between the two guanidine groups is 67.86 (1)°.

Comment

An *N*-substituted derivative of biguanide, metformin (*N,N*-dimethylbiguanide), is a powerful oral antihyperglycaemic drug that has been used in many countries for over 30 years for treating diabetic patients with non-insulin-dependent diabetes mellitus. As an *N*-donor monodentate and bidentate ligand, it also forms complexes with many metal ions (Bailey, 1992; Ray, 1961). Zinc is considered an important inorganic chemical element involved in biological processes. It exists in many organs, such as the liver, kidney, brain and pancreas, and it has an important role and function within proteins, enzymes, and so on.
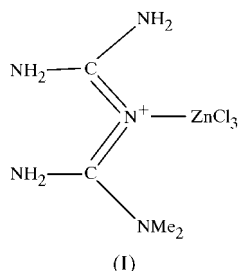
From a chemical point of view, biguanide and its *N*-substituted derivatives are considered to be a good type of chelating ligand, with abundant chemical properties. There are structural differences between monodentate and bidentate ligands when they coordinate to different metal ions, with the former normally forming a tetrahedron and the latter a square-planar configuration, *e.g.* the bidentate biguanide-derivative complexes of Co^{II}, Tc^{V}, Rh^{V}, Ag^{III} and Cu^{II} all have a square-planar geometry (Lemoine *et al.*, 1996; Marchi *et al.*, 1999;

Ghosh *et al.*, 1994; Hota & Saha, 1984). In addition, the planar angle between the two guanidine groups differs between complexes with monodentate or bidentate ligands. In the light of this, the title compound, (I), with a monodentate biguanide ligand, has been prepared, and its crystal structure is presented here.

The geometric parameters of (I) are listed in Table 1 and the molecular structure is illustrated in Fig. 1. The structure can be viewed as two parts, namely C$_4$H$_{12}$N$_5$$^+$ and ZnCl$_3$$^-$. These two parts are connected through the formation of a Zn—N coordination bond of 2.0611 (14) Å.

In the structure of (I), each Zn^{2+} cation is coordinated by one N atom of the biguanide ligand and three Cl$^-$ ions, in a slightly distorted tetrahedral configuration. The Cl—Zn bond distances are almost equal; range 2.2568 (7)–2.2728 (6) Å, with a mean of 2.2622 Å. These values are compatible with the Co—Cl bond lengths in [CoCl$_3$(C$_4$H$_{12}$N$_5$)] [2.250 (1)–2.264 (1) Å; Lemoine *et al.*, 1996]. The Cl—Zn distances in (I) are also in agreement with those found in a morpholine biguanide-coordinated Zn complex, [ZnCl$_3$(C$_6$H$_{14}$N$_5$O)] (Yang & Zhu, 1991, 1992), in which the Cl—Zn bond distances [2.245 (1)–2.258 (1) Å] are slightly shorter than those in (I).

The Cl—Zn—Cl angles in (I) are in the range 109.82 (3)–116.50 (3)°, and the Cl—Zn—N angles are in the range 104.43 (4)–108.45 (4)°, close to the theoretical tetrahedral value of 109.5°.
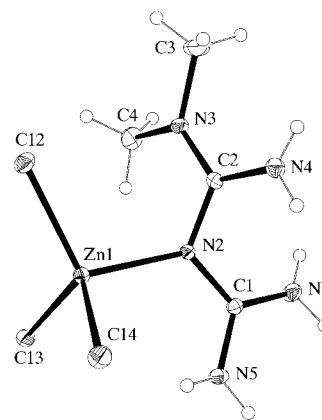
Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
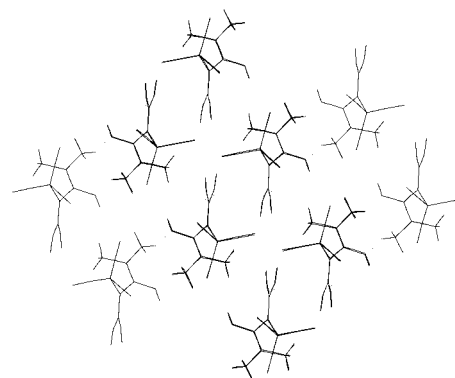
Figure 2
A packing diagram of (I) viewed along the *b* axis.

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In the crystal structure of metformin hydrochloride, Hariharan *et al.* (1989) pointed out that the C—N bond distances in the two guanide groups are intermediate between single and double bonds, in the range 1.330 (4)–1.348 (3) Å. A similar conclusion can be drawn for the C—N bond characterization in (I), with C—N bond lengths in the range 1.314 (2)–1.382 (2) Å. The standard single and double C—N bond lengths are 1.474 and 1.265 Å, respectively (Lide, 1962).

The two halves of the biguanide residue in (I) are planar, with atom C1 0.033 Å out of the N1/N2/N5 plane and atom C2 0.042 Å out of the N2/N3/N4 plane. The planes of the two different halves form a dihedral angle of 67.86° in (I); dihedral angles of 77.58 and 67.9 (1)° were found in [ZnCl3(C6H14N5O)] (Yang & Zhu, 1992) and metformin hydrochloride (Hariharan *et al.*, 1989), respectively. Thus, the dihedral angle in (I) is very close to that of the uncomplexed biguanide. It is noted that the different *N*-substituted group within the ligand is the main reason for the variation in the dihedral angle; the dihedral angle in the morpholine-substituted complex is approximately 9.72° larger than that in the dimethyl-substituted complex.

Experimental

Crystals of (I) were grown from an aqueous solution of zinc dichloride dihydrate (1.0 mmol) and *N,N*-dimethylbiguanide hydrochloride (1.0 mmol). The solution was left at room temperature and crystals formed in the bottom of the flask after 1–3 months. The elemental analyses were in agreement with the structural composition of (I).

Crystal data

$[ZnCl_3(C_4H_{12}N_5)]$
$M_r = 301.91$
Monoclinic, $P2_1/c$
$a = 12.5040 (7)$ Å
$b = 7.5170 (5)$ Å
$c = 13.0894 (5)$ Å
$\beta = 113.237 (3)°$
$V = 1130.5 (1)$ Å^3
$Z = 4$

$D_x = 1.774$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 407 reflections
$\theta = 3.1–27.5°$
$\mu = 2.85$ mm^{-1}
$T = 173 (2)$ K
Block, colourless
$0.4 \times 0.3 \times 0.2$ mm

Data collection

Rigaku R-AXIS RAPID image-plate diffractometer
Oscillation scans
Absorption correction: empirical (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.402$, $T_{max} = 0.566$
10 407 measured reflections
2574 independent reflections

2107 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 15$
Intensity variation: $\pm 1\%$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.048$
$S = 0.94$
2574 reflections
138 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

H atoms attached to C atoms were treated as riding, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}$ of the parent atom. H atoms on N atoms

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	2.0611 (14)	N2—C2	1.382 (2)
Zn1—Cl3	2.2568 (7)	N3—C2	1.314 (2)
Zn1—Cl2	2.2570 (5)	N3—C4	1.459 (2)
Zn1—Cl4	2.2728 (6)	N3—C3	1.465 (2)
N1—C1	1.328 (2)	N4—C2	1.334 (2)
N2—C1	1.359 (2)	N5—C1	1.320 (2)
N2—Zn1—Cl3	107.05 (4)	C2—N3—C4	122.38 (15)
N2—Zn1—Cl2	108.45 (4)	C2—N3—C3	121.16 (16)
Cl3—Zn1—Cl2	116.50 (3)	C4—N3—C3	116.02 (15)
N2—Zn1—Cl4	104.43 (4)	N5—C1—N1	119.29 (16)
Cl3—Zn1—Cl4	109.82 (3)	N5—C1—N2	118.71 (16)
Cl2—Zn1—Cl4	109.86 (2)	N1—C1—N2	121.86 (15)
C1—N2—C2	118.68 (14)	N3—C2—N4	120.89 (16)
C1—N2—Zn1	121.78 (11)	N3—C2—N2	119.69 (15)
C2—N2—Zn1	117.15 (11)	N4—C2—N2	119.13 (15)
Zn1—N2—C1—N5	−8.2 (2)	C3—N3—C2—N4	−7.6 (3)
Zn1—N2—C1—N1	167.41 (13)	N3—C2—N2—C1	134.46 (17)
Zn1—N2—C2—N4	111.06 (16)	N1—C1—N2—C2	−30.7 (2)
Zn1—N2—C2—N3	−62.77 (19)	N5—C1—N2—C2	153.77 (16)
Cl4—Zn1—N2—C2	−107.20 (12)	N3—C2—N4—N2	173.8 (3)
Cl2—Zn1—N2—C2	9.91 (13)	N2—C1—N1—N5	−175.5 (3)
Cl3—Zn1—N2—C2	136.37 (11)		
C4—N3—C2—N4	164.46 (17)		

were refined with $U_{iso}(H) = 0.08$ Å^2 and N—H distances in the range 0.78–0.92 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *SHELXS*97 (Sheldrick, 1997); program(s) used to solve structure: *SHELXS*97; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990).

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