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Dichlorobis(imidazolidin-2-one-κO)-zinc(II) at 150 K

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In the title compound, $[ZnCl_2(C_3H_6N_2O)_2]$, the zinc(II) cation is surrounded by a distorted tetrahedral environment consisting of two Cl anions and two imidazolidin-2-one molecules, the latter bound to the metal through their carbonyl O atoms. All atoms that are able to participate in hydrogen bonding are involved in such interactions. A hydrogen-bonding network mediates the formation of molecular columns parallel to the *a* axis. Neighboring columns are not bound by significant non-covalent interactions; the result is an extended pattern of supramolecular aggregation that is intermediate in completeness between the situations observed in two related complexes of cobalt that have been studied previously.

Comment

The cyclic organic moiety imidazolidin-2-one (HimiO), derived from urea, is widely used in organic chemistry. Its derivatives, along with some organic molecules of which this moiety is a fragment, are used in the synthesis of amino acids (Seebach *et al.*, 1991), antibiotics and antiseptics (Pereira *et al.*, 1996). An entire range of weed killers is derived from this compound (Tseng *et al.*, 1991). HimiO is also utilized in the synthesis of lactones and lactams with rhodium catalysts (Doyle & Kalinin, 1995). The most interesting characteristics of this compound, from the point of view of coordination chemistry, are its three functionalized positions, *viz*. two amide groups and one carbonyl fragment, which are disposed in such a way as to enable the formation of both intra- and intermolecular hydrogen bonds by complexes in which HimiO is a ligand. In spite of the potential synthetic importance of this moiety as a ligand and its demonstrated utility in other contexts, HimiO has not been used extensively in *d*-block chemistry. To date, complexes of HimiO with cadmium (Brown *et al.*, 1972), mercury (Majeste & Trefonas, 1972), copper (Majeste & Trefonas, 1974), tin (Tavridou *et al.*, 1993, 1995) and uranium (Mikhailov *et al.*, 1999) have been structurally characterized.

We have recently reported the preparation of two cobalt(II) complexes of HimiO, which, in their respective crystals, possess discrepant degrees of completeness in their hydrogen-bonding interactions (Falvello *et al.*, 2003). The first complex isolated, namely blue $[Co(HimiO)_6][CoCl_4]$, (II), which is stable under mild environmental conditions, possesses an incomplete hydrogen-bonding pattern. Under forcing conditions, it evolves into the stable pink heteroleptic compound $[Co(HimiO)_4(H_2O)_2]Cl_2\cdot 2(HimiO)$, (III), which, in the solid state, possesses a complete hydrogen-bonding pattern, that is, one in which all possible donors and acceptors are employed. Both the aqua ligands and the free imidazolidin-2-one molecules in (III) play important roles in the extended crystal structure, and the formation of a stronger hydrogen-bonding pattern than that found in (II) was taken to be the driving force for the evolution of the system.

These results suggested the potential interest of a further study involving a d^{10} metal center, namely Zn^{II}. With no intrinsic steric preference residing on the metal, the product isolated would reflect to a greater degree the non-covalent binding properties of HimiO itself and was expected to be an important element in a more complete characterization of this polyfunctional ligand.

Zn^{II} is an eminently useful species in parametric topological studies involving polyfunctional ligands in coordination chemistry because, as alluded to above, its $3d^{10}$ electronic configuration and the concomitant lack of ligand-field stabilization energy obviate any geometric shape preference, so the stereochemistry of the complexes formed depends on such parameters as the sizes of the ligands, the electrostatic forces present, and the relative strengths of the covalent bonds and non-covalent interactions formed.

The crystal structure of $[ZnCl_2(HimiO)_2]$, (I), is different from that found in either of the Co^{II} compounds (II) and (III), as was expected. The structure of (I) also differs from that found in HimiO complexes with other d^{10} metals, such as cadmium (Brown *et al.*, 1972), which forms a complex with a structure similar to that of (II), and mercury (Majeste & Trefonas, 1972). The central metal in (I) has a distorted tetrahedral coordination environment, formed by two chloro ligands and two neutral *O*-coordinated HimiO moieties (Fig. 1). The Zn—Cl distances (Table 1) are similar to those found in other tetrahedral Zn^{II} compounds (Cingi *et al.*, 1972; Herceg & Fischer, 1974; Suzuki *et al.*, 1991), but the Zn—O contacts are slightly shorter (Nardelli *et al.*, 1963; Fusch & Lippert, 1994; Yar & Lessinger, 1995). The Cl1—Zn—Cl2 angle is greater than the O1—Zn—O6 angle, presumably because of the steric requirements of the chloro ligands. The carbonyl C═O distance is similar to that observed in the structure of the unligated ligand in imidazolidin-2-one hemihydrate [1.262 (4) Å; Kapon & Reisner, 1989]. It can therefore be concluded that the formation of the Zn—O bond is not accompanied by significant changes in the electronic structure of the carbonyl group. However, the structure of $[HgCl_2(HimiO)_2]$, which could be expected to be isotypic with (I)

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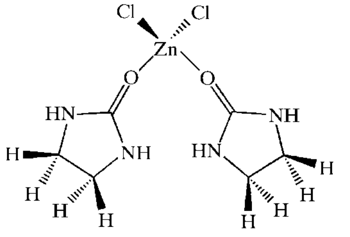
because they have the same molecular formula, is completely different. The central Hg atom has a square coordination geometry, formed by the two chloro and two *O*-coordinated HimiO moieties. One N atom of each HimiO ligand forms a long contact with Hg atoms of neighboring complexes, so the metal can be regarded as having a distorted octahedral coordination. These structural features influence the HimiO molecule, which is asymmetrically distorted, with different distances for the two N—C(=O) bonds (Majeste & Trefonas, 1972).



(I)

All of the functionalized positions of the imidazolidin-2-one ligands in (I) participate in hydrogen bonds. Two intramolecular hydrogen bonds are present (Table 2), *viz*. one involving two HimiO ligands (N10—H10···O1) and one between an amide group of the HimiO molecule and a chloro ligand (N2—H2···Cl1). An extensive intermolecular hydrogen-bond network connects neighboring molecules. The three-dimensional structure is further stabilized by a series of short contacts between the ethylene CH groups and both the Cl atoms and the carbonyl O atoms (Fig. 2). This hydrogen-bond pattern differs notably from that found in the Co^{II} HimiO complexes. In (II), the functionalized positions of the HimiO ligands are directed toward the metal center, and so they are hindered with respect to participation in intermolecular hydrogen bonds. In (III), however, the presence of water molecules in the coordination sphere, along with unligated HimiO molecules, enables the formation of a strong hydrogen-bonding pattern. In the latter case, the molecules are arranged in columns that are connected through the free HimiO molecules. In (I), an intermediate situation is found. The hydrogen-bond network connects neighboring molecular

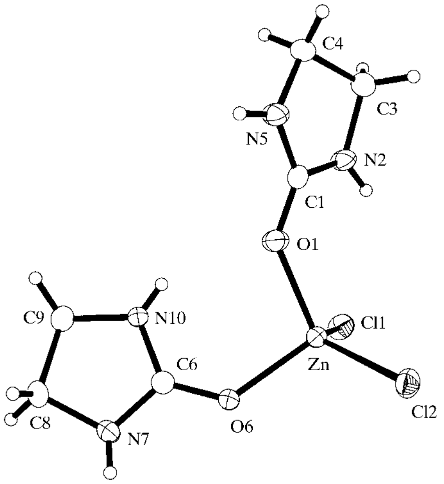


Figure 1
A displacement ellipsoid plot of (I). Non-H atoms are represented by 50% probability ellipsoids and H atoms are shown as small circles of arbitrary size.

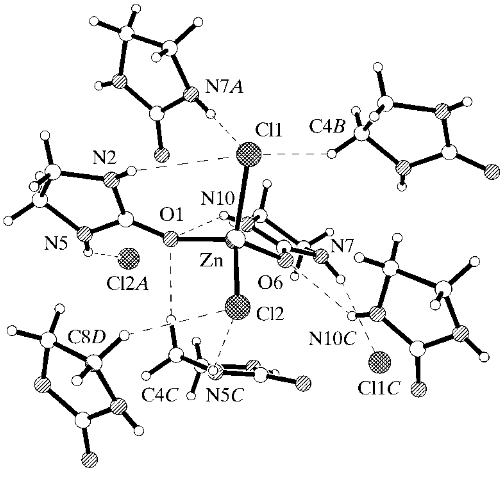


Figure 2
The intra- and intermolecular hydrogen-bonding arrangement in (I). [Symmetry codes: (*A*) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (*B*) $1+x, y, z$; (*C*) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (*D*) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$.]

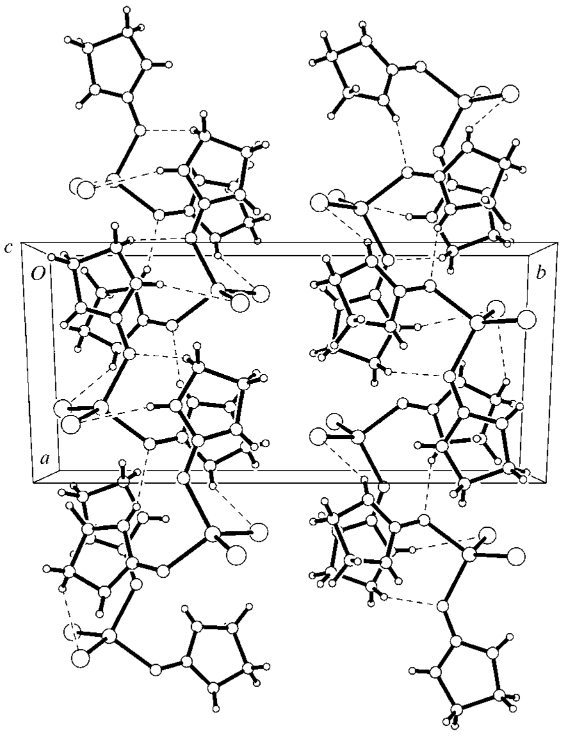


Figure 3
A partial view of the crystal packing in (I), showing the orientation inside the cell of the columns formed by the hydrogen-bonding interactions.

units, mediating the formation of columns that extend parallel to the *a* axis of the cell, similar to the situation in (III). In (I), however, these columns are independent entities and are not connected by hydrogen bonds (Fig. 3). This three-dimensional organization into independent infinite chains is the only feature that the Hg and Zn HimiO complexes have in common. The arrangement of the complexes within the chains is completely different in the two cases.

The two previously reported Co^{II} complexes and the present structure of (I), taken together, form a group with sets of hydrogen bonds that are progressively more complete. Complex (II) possesses unrequited hydrogen-bonding capability in the crystal and can be made to evolve into (III), in which all hydrogen-bonding potential is expressed. The Zn-centered complex (I) is an intermediate case, with a complete enough set of non-covalent interactions to confer long-term stability to the crystals, even though hydrogen bonds do not bind neighboring molecules in all directions.

Experimental

Imidazolidin-2-one (purchased from Aldrich) was added, in a 2:1 molar ratio, to a solution of $ZnCl_2$ in propan-2-ol (20 ml). The white powder obtained from this reaction was washed with *n*-hexane in order to dry it. Crystals of (I) were obtained by slow addition, at room temperature, of *n*-hexane to a saturated solution of the zinc complex in acetone.

Crystal data

$[ZnCl_2(C_3H_6N_2O)_2]$
$M_r = 308.47$
Monoclinic, $P2_1/n$
$a = 8.4717$ (6) Å
$b = 17.0289$ (10) Å
$c = 8.5571$ (7) Å
$\beta = 112.784$ (6)°
$V = 1138.15$ (14) Å^3
$Z = 4$
$D_x = 1.800$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.3$–15.8°
$\mu = 2.61$ mm^{-1}
$T = 150$ (1) K
Plate, colorless
0.33 × 0.27 × 0.14 mm

Data collection

Nonius CAD-4 diffractometer
ω–$\frac{1}{3}\theta$ scans
Absorption correction: φ scan (Kopfmann & Huber, 1968)
$T_{min} = 0.479$, $T_{max} = 0.711$
3447 measured reflections
2599 independent reflections
2210 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$

$\theta_{max} = 27.5°$
$h = -6 \rightarrow 10$
$k = 0 \rightarrow 22$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 180 min
intensity decay: 5%

Table 1
Selected geometric parameters (Å, °).

Zn—O1	1.9748 (18)	Zn—Cl2	2.2122 (7)
Zn—O6	1.9801 (17)	Zn—Cl1	2.2213 (7)
O1—Zn—O6	99.22 (7)	O1—Zn—Cl1	107.04 (6)
O1—Zn—Cl2	113.41 (6)	O6—Zn—Cl1	112.47 (6)
O6—Zn—Cl2	105.37 (5)	Cl2—Zn—Cl1	117.84 (3)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.067$
$S = 1.04$
2599 reflections
184 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.0132P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl1	0.80 (3)	2.91 (3)	3.533 (2)	136 (3)
N5—H5···Cl2^{i}	0.80 (3)	2.79 (3)	3.481 (2)	145 (3)
N7—H7···Cl1^{ii}	0.83 (3)	2.65 (3)	3.402 (2)	151 (3)
N10—H10···O6^{i}	0.75 (3)	2.39 (3)	2.990 (3)	138 (3)
N10—H10···O1	0.75 (3)	2.39 (3)	2.987 (3)	137 (3)
C4—H41···O1^{i}	0.95 (3)	2.46 (3)	3.336 (3)	152 (2)
C4—H42···Cl1^{iii}	0.97 (3)	2.92 (3)	3.693 (3)	137 (2)
C8—H81···Cl1^{iv}	0.99 (3)	2.91 (3)	3.482 (3)	118 (2)
C8—H81···Cl2^{v}	0.99 (3)	2.81 (3)	3.673 (3)	146 (2)

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

All H atoms were found in a difference Fourier map, and their positions and isotropic displacement parameters were refined freely [C—H = 0.93 (3)–0.99 (3) Å].

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1996); cell refinement: *CAD*-4/*PC*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1145). Services for accessing these data are described at the back of the journal.

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