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Bis(acetato-*O*)bis(urea-*O*)zinc(II), [Zn(H₂NCONH₂)₂(CH₃COO)₂]

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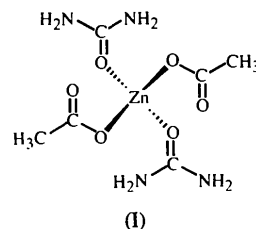
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Abstract

The title molecular complex, [Zn(C₂H₃O₂)₂(CH₄N₂O)₂], crystallized from an aqueous solution of urea and zinc acetate in a 2:1 ratio. Zn^{II} is coordinated by four O atoms in a systematically distorted tetrahedral arrangement, while the complex as a whole has an approximate twofold rotation axis. Each urea ligates *via* its carbonyl O atom, while each acetate is monodentate. Each non-ligating carbonyl O atom of the acetate ligands accepts an intramolecular hydrogen bond from urea. Intermolecular hydrogen bonds give rise to a layer structure, with the layers stacked by van der Waals attractions only.

Comment

Homogeneous precipitation of substances insoluble in basic solution, accomplished by the decomposition of urea to NH₃ and CO₂, is a well known technique used for the preparation of various insoluble basic salts of transition metals, including some salts containing Zn^{II} and acetate. One such experiment, however, starting with a 2:1 ratio of urea to zinc acetate, in almost saturated aqueous solution, yielded crystals which were soluble in water. IR and NMR spectral evidence indicated the probable presence of urea as well as acetate ligands. The density of the crystal and its unit-cell parameters gave a likely formula of [Zn(H₂NCONH₂)₂(CH₃COO)₂], (I), which was confirmed by the present X-ray structure determination.



The title molecular complex, (I) (Fig. 1), has Zn^{II} coordinated by four O atoms in a systematically distorted tetrahedral arrangement, while the complex as a whole has an approximate twofold rotation axis. The degree of distortion from a regular tetrahedron is severe, with O—Zn—O angles ranging from 89.5 to 126.8° (see Table 2).

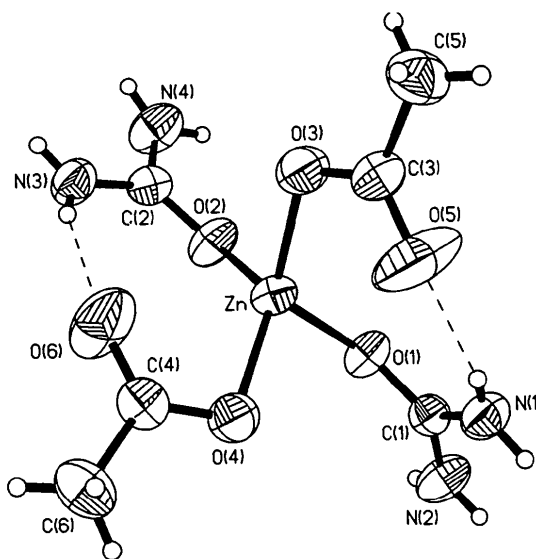


Fig. 1. The title molecular complex, viewed down its approximate twofold axis, showing 50% probability displacement ellipsoids.

In (I), urea binds as a monodentate ligand through its carbonyl O atom, as is also seen in hexakis(urea)-zinc(II) nitrate (van de Giesen & Stam, 1972). The title complex is a neutral tetrahedral molecular complex and the urea O—Zn distances [1.997 (2) and 1.994 (2) Å] are significantly shorter than the three independent O—Zn distances in the octahedral [Zn(urea)₆]²⁺ cation [2.147 (2), 2.073 (3) and 2.091 (3) Å]. However, the urea—Zn—urea O—Zn—O angle of 89.5 (1)° in (I) is intermediate in the range 84.6–96.5° for the seven independent O—Zn—O angles in the hexakis(urea)zinc ion. Moreover, in both complexes, urea binds with a characteristic C=O···Zn angle, *i.e.* in (I), 128.0 (2) and 130.4 (2)°, and in the hexakis(urea)zinc(II) ion,

129.7, 132.3 and 132.8°. Both urea molecules in (I), including all H atoms, are essentially planar; r.m.s. and maximum deviations from planarity are 0.013 and 0.028 Å, respectively, for one urea, and 0.051 and 0.103 Å for the other. The two urea planes form an angle of 64.7° with respect to each other. In (I), Zn is displaced from the urea planes by 0.998 and 1.043 Å; in the hexakis(urea)zinc(II) ion, these deviations are 0.079, 0.834 and 1.146 Å.

The acetate ligands are both definitely monodentate in (I); the ligating O—Zn distances are 1.970 (2) and 1.995 (2) Å, with an O—Zn—O angle of 121.1 (1)°, while the non-ligating carbonyl O···Zn distances are 2.699 (3) and 2.576 (3) Å. In anhydrous Zn^{II} acetate (Capilla & Aranda, 1979), each Zn ion is in a slightly distorted tetrahedral environment in a three-dimensional polymeric network. Each acetate acts as a bidentate ligand bridging two Zn ions, with O—Zn distances of 1.914 (11), 1.929 (12), 1.937 (12) and 1.955 (11) Å, shorter than those found in (I), and O—Zn—O angles ranging from 102.2 (5) to 115.9 (6)°, resulting in a much more regular tetrahedral environment than in (I). By comparison, in zinc acetate dihydrate, [Zn(CH₃COO)₂(H₂O)₂] (van Niekerk, Schoening & Talbot, 1953), in which the molecule lies on a crystallographic twofold rotation axis and Zn is six-coordinate, each acetate acts as a bidentate chelating ligand, with significantly longer O—Zn distances of 2.18 and 2.17 Å. In the tetrahedral tetranuclear molecular cluster zinc oxyacetate (or 'basic zinc acetate'), [Zn₄O(CH₃COO)₆] (Koyama & Saito, 1954), each acetate acts as a bidentate ligand bridging two Zn ions, with both O—Zn distances 1.98 Å, nearly the same as those in (I).

A molecule closely related to (I) is the thiourea analog [Zn(H₂NCSNH₂)₂(CH₃COO)₂] (Cavalca, Gasparri, Andreotti & Domiano, 1967), in which Zn is also four-coordinate, in a systematically distorted tetrahedron consisting of two S atoms from thiourea molecules and two O atoms from two monodentate acetate ligands [O—Zn distances 1.973 (6), 2.996 (5) and 1.954 (8), 2.891 (9) Å; O—Zn—O 101.0 (3) and S—Zn—S 114.3 (1)°]. The overall crystal structure of this thiourea analog is completely different from that of (I), while the molecule itself, though quite similar, is not entirely isostructural with (I) either. Among other differences, it has only one intramolecular N—H···O hydrogen bond rather than the two seen in (I).

The geometric data pertinent to understanding the hydrogen-bonding scheme are given in Table 3. (We realize that X-ray refinement of H systematically underestimates the N—H internuclear distances and thus also overestimates the H···O distances.) There are two intramolecular hydrogen bonds [N(1)···O(5) and N(3)···O(6)], where one N atom of each urea donates to the non-ligating carbonyl O atom of an adjacent acetate (Fig. 1). These hydrogen bonds may play a major role in making the coordination around Zn tetrahedral rather

than octahedral, by keeping the acetates monodentate rather than bidentate.

On either side of every molecular complex in the crystal, both N atoms of a urea hydrogen bond to the same ligating O atom of an acetate group in an inversion-related molecule [N(1)···O(4ⁱ), N(2)···O(4ⁱ) and N(3)···O(3ⁱⁱⁱ), N(4)···O(3ⁱⁱⁱ)]; see Table 3 for symmetry codes], forming ribbons parallel to the [111] direction (Fig. 2). These ribbons are linked side-by-side by further pairs of hydrogen bonds around inversion centers, between atom N(2) of one urea and the carbonyl O(1) atom of another urea [N(2)···O(1ⁱⁱ)], to form sheets. The N(2)···O(2ⁱⁱ) distance of 3.007 Å between the same two molecules might indicate a three-center (bifurcated) hydrogen bond here, but the long H(21)···O(2ⁱⁱ) distance and the small N(2)—H(21)···O(2ⁱⁱ) angle suggest that this interaction is weak or negligible. One further potential hydrogen bond between atom N(4) and the acetate carbonyl O(5^{iv}) atom of a translationally related molecule must also be very weak or negligible, because the N···O and H···O distances are so long.

The hydrogen-bonded layers (Fig. 2), parallel to and halfway between the (011) planes, are stacked upon one another by translation and held together by van der Waals attractions only.

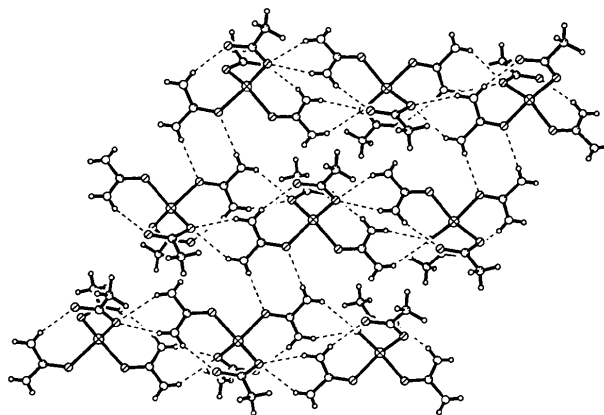


Fig. 2. The packing of the molecules in the hydrogen-bonded layer.

Experimental

Solid [Zn(H₂NCONH₂)₂(CH₃COO)₂] was initially synthesized by evaporation of an aqueous solution containing urea and zinc acetate in a 2:1 ratio, and was recrystallized from water. The crystal density D_m was measured by flotation in a mixture of C₂H₄Cl₂ and C₂H₄Br₂.

Crystal data

[Zn(C₂H₃O₂)₂(CH₄N₂O)₂]
 $M_r = 303.58$

Mo K α radiation
 $\lambda = 0.71069 \text{ \AA}$

Triclinic

$P\bar{1}$
 $a = 7.467(2) \text{ \AA}$
 $b = 8.161(3) \text{ \AA}$
 $c = 10.717(2) \text{ \AA}$
 $\alpha = 80.81(2)^\circ$
 $\beta = 73.64(2)^\circ$
 $\gamma = 71.71(2)^\circ$
 $V = 593.1 \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.700 \text{ Mg m}^{-3}$
 $D_m = 1.69(1) \text{ Mg m}^{-3}$

Cell parameters from 15 reflections

$\theta = 4.43\text{--}12.69^\circ$
 $\mu = 2.09 \text{ mm}^{-1}$
 $T = 297 \text{ K}$
 Block
 $0.38 \times 0.25 \times 0.20 \text{ mm}$
 Colorless

Data collection

Nicolet P3 diffractometer
 Wyckoff ω scans
 Absorption correction:
 ψ scans of 6 reflections
 (North, Phillips &
 Mathews, 1968)
 $T_{\min} = 0.554$, $T_{\max} =$
 0.726
 2265 measured reflections
 2088 independent reflections

1786 observed reflections
 $[F_o > 4\sigma(F_o)]$
 $R_{\text{int}} = 0.0198$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = 0 \rightarrow 12$
 2 standard reflections
 monitored every 100
 reflections
 intensity decay: <2.0%

Refinement

Refinement on F^2
 $R(F) = 0.0423$
 $wR(F^2) = 0.0806$
 $S = 1.052$
 2088 reflections
 211 parameters
 All H-atom parameters
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2$
 $+ 0.257P]$
 where $P = [\max(F_o^2, 0)$
 $+ 2F_c^2]/3$

$(\Delta/\sigma)_{\text{max}} = 0.062$
 $[\text{y of H(63)}]$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
 Extinction correction:
 $F_c^* = F_c[1 + (7.93$
 $\times 10^{-6}F_c^2/\sin 2\theta)]^{-1/4}$
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C)

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

Zn—O(1)	1.997(2)	Zn—O(2)	1.994(2)
Zn—O(3)	1.970(2)	Zn—O(4)	1.995(2)
O(1)—C(1)	1.270(4)	O(2)—C(2)	1.256(4)
C(1)—N(1)	1.319(4)	C(2)—N(3)	1.315(4)
C(1)—N(2)	1.325(4)	C(2)—N(4)	1.337(4)
O(3)—C(3)	1.258(4)	O(4)—C(4)	1.265(4)
C(3)—O(5)	1.214(4)	C(4)—O(6)	1.221(4)
C(3)—C(5)	1.490(5)	C(4)—C(6)	1.491(5)
O(1)—Zn—O(2)	89.5(1)	O(3)—Zn—O(4)	121.1(1)
O(2)—Zn—O(3)	97.8(1)	O(1)—Zn—O(4)	98.1(1)
O(1)—Zn—O(3)	121.1(1)	O(2)—Zn—O(4)	126.8(1)
C(1)—O(1)—Zn	128.0(2)	C(2)—O(2)—Zn	130.4(2)
O(1)—C(1)—N(1)	122.5(3)	O(2)—C(2)—N(3)	122.6(3)
O(1)—C(1)—N(2)	119.2(3)	O(2)—C(2)—N(4)	119.0(3)
N(1)—C(1)—N(2)	118.3(3)	N(3)—C(2)—N(4)	118.3(3)
C(3)—O(3)—Zn	111.3(2)	C(4)—O(4)—Zn	106.0(2)
O(3)—C(3)—O(5)	119.9(3)	O(4)—C(4)—O(6)	120.2(3)
O(3)—C(3)—C(5)	118.5(3)	O(4)—C(4)—C(6)	118.6(3)
O(5)—C(3)—C(5)	121.5(4)	O(6)—C(4)—C(6)	121.2(4)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\cdots H\cdots A$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N(1)—H(11)···O(5)	2.16(4)	2.900(5)	165(4)
N(1)—H(12)···O(4 ⁱ)	2.31(4)	3.055(4)	154(3)
N(2)—H(22)···O(4 ⁱ)	2.46(4)	3.137(5)	147(4)
N(2)—H(21)···O(1 ⁱⁱ)	2.34(4)	3.079(4)	167(4)
N(2)—H(21)···O(2 ⁱⁱ)	2.65(4)	3.007(4)	111(2)
N(3)—H(31)···O(6)	2.12(4)	2.865(5)	160(4)
N(3)—H(32)···O(3 ⁱⁱⁱ)	2.28(4)	2.991(4)	157(4)
N(4)—H(42)···O(3 ⁱⁱⁱ)	2.51(4)	3.151(5)	143(4)
N(4)—H(41)···O(5 ^{iv})	2.58(4)	3.382(6)	160(4)

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

The Zn atom was located initially from a Patterson function, then all C, N and O atoms were located in successive Fourier syntheses. Finally all H atoms were located in successive difference Fourier syntheses. Refinement was by full-matrix least squares and the function minimized was $\sum w(F_o^2 - F_c^2)^2$, where F_o^2 may be (statistically) negative. Zn, C, N and O atoms were refined anisotropically and H atoms isotropically, with no geometric constraints. Computer programs used were *SHELXS86* (Sheldrick, 1985) and *SHELXL93* (Sheldrick, 1993).

We wish to thank Professor G. Parkin, Chemistry Department, Columbia University, for collecting the X-ray diffraction data, and Professor J. Clardy, Chemistry Department, Cornell University, for the use of his computational facilities. OY was supported by a student summer research stipend from the Howard Hughes Medical Institute Science Pipeline Project.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z	U_{eq}
Zn	0.2349(1)	0.2512(1)	0.2470(1)	0.037(1)
O(1)	0.1327(3)	0.4568(3)	0.1318(2)	0.042(1)
C(1)	0.2197(4)	0.5655(4)	0.0656(3)	0.037(1)
N(1)	0.3335(5)	0.6241(4)	0.1105(3)	0.047(1)
N(2)	0.1938(5)	0.6251(5)	-0.0525(3)	0.053(1)
O(2)	0.0018(3)	0.1727(3)	0.2619(2)	0.049(1)
C(2)	-0.0566(4)	0.0531(4)	0.3342(3)	0.038(1)
N(3)	0.0625(5)	-0.0982(4)	0.3597(3)	0.049(1)
N(4)	-0.2475(5)	0.0781(5)	0.3849(4)	0.057(1)
O(3)	0.1992(4)	0.2694(4)	0.4341(2)	0.056(1)
C(3)	0.2808(5)	0.3745(4)	0.4513(3)	0.043(1)
O(5)	0.3812(6)	0.4374(6)	0.3584(3)	0.113(2)
C(5)	0.2614(8)	0.4095(8)	0.5874(4)	0.061(1)
O(4)	0.4996(3)	0.1640(3)	0.1306(2)	0.053(1)
C(4)	0.5538(4)	0.0028(4)	0.1603(3)	0.042(1)
O(6)	0.4472(4)	-0.0659(4)	0.2457(4)	0.091(1)
C(6)	0.7505(6)	-0.0994(7)	0.0908(5)	0.061(1)

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4,4'-Oxydianilinium Tetrachlorocadmate(II), an Intercalation Compound

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Abstract

The title compound, $(C_{12}H_{14}N_2O)[CdCl_4]$, is a typical two-dimensional organic intercalated compound. The inorganic layers of the compound are formed by $CdCl_6$ octahedra sharing corner Cl atoms (*i.e.* *catena*-poly[dichlorocadmium-di- μ -chloro]). The organic diammonium cations are intercalated between every two metal–halogen layers and form the organic layers of the compound through hydrogen bonding.

Comment

Molecular assembling has recently become an exciting research field because it is a key technique in the development of new materials. The title compound, (I), belongs to the family of layer perovskites that have the general formula $(NH_3-R)_2MCl_4$ or $(NH_3-R'-NH_3)MCl_4$ ($M = Cd, Mn, Cr, Cu, Fe, Pt, Pd$). Around 20 years ago many layer perovskites in which group R is C_nH_{2n+1} and R' is C_nH_{2n} were investigated with respect to their thermal and magnetic properties (Arend & Huber, 1978; Needham & Willett, 1984). We found that the structure of this kind of compound is very similar

to that of a Langmuir–Blodgett film and seems to offer a new route to two-dimensional molecular assemblies. In this paper we report the crystal structure of the title salt, (I).

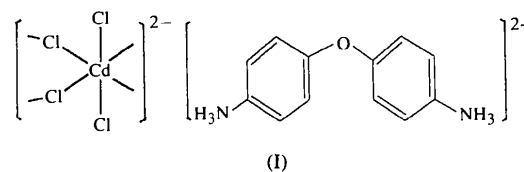


Fig. 1 shows the atom-numbering scheme and Fig. 2 shows the packing of the ions in the unit cell. It can be seen from Fig. 2 that the structure of the title compound consists of two types of layers: metal–halogen layers and organic diammonium layers. The metal–halogen layer is formed by $CdCl_6$ octahedra sharing corners in the xy plane of the crystal cell; the stoichiometry of the layer is $[CdCl_4]_n^{2n-}$. The $-NH_3^+$ groups of each 4,4'-oxydianilinium cation are positioned in the 'hole' enclosed by four $CdCl_6$ octahedra. The 4,4'-oxydianilinium ions are sandwiched between two metal–halogen layers and form organic layers. These layers stack on top of each other, forming a two-dimensional structure which is similar to that of the Langmuir–Blodgett film.

In the $CdCl_6$ octahedron, the distance of the Cd atom to the bridging Cl(2) atoms is significantly longer (*ca* 0.12 Å) than that of the Cd atom to the axial Cl(1) atoms. The $CdCl_6$ octahedron is therefore compressed. Each $-NH_3^+$ group of the 4,4'-oxydianilinium ion is surrounded by four Cl(1) and four Cl(2) atoms. The distances of an N atom to one Cl(2) and to two Cl(1) atoms are 3.257 (5), 3.158 (4) and 3.168 (4) Å, respectively; these are all quite reasonable N–H...Cl hydrogen-bonding distances. As a result of hydrogen bonding, the bonded Cl atoms are brought closer to the N atom and the $CdCl_6$ octahedron is tipped *ca* 9.3 (4)° out of the xy plane of the crystal cell. This results in puckering of the metal–halogen layers, as shown in Fig. 2. The Cd–Cl–Cd bond is not linear but forms an angle of 152.19 (4)° and the dihedral angle between the two benzene rings of the 4,4'-oxydianilinium ion is 73.22 (4)°.

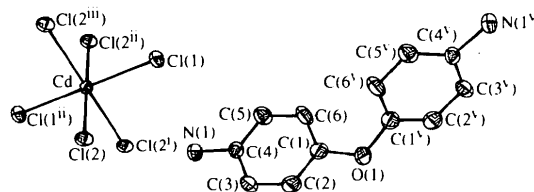


Fig. 1. The numbering of the atoms of the title compound. Displacement ellipsoids are plotted at the 30% probability level. H atoms are omitted for clarity.