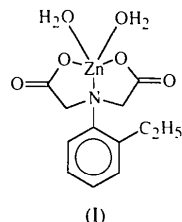Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Zeleňák, V., Györyová, K. & Čísařová, I. (1995). *Main Group Met. Chem.* **18**, 211–216.

(I)

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Diaqua(2-ethylphenyliminodiacetato-N,O,O')zinc(II)

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Abstract

The title complex, $[Zn(C_{12}H_{13}NO_4)(H_2O)_2]$, has a coordination polyhedron around the Zn^{II} atom that can be described as a square-based pyramid strongly distorted towards a trigonal bipyramid. The basal plane is defined by one N and two O atoms belonging to the tridentate ligand and one water O atom, while the axial position is occupied by another water O atom. The discrete molecules are grouped through hydrogen bonding into parallel double layers with the phenyl groups pointing outwards.

Comment

The crystal structure of the title zinc complex, (I), is made up of discrete neutral $[Zn(L)(H_2O)_2]$ molecules, H_2L being 2-ethylphenyliminodiacetic acid. These discrete molecules are assembled through hydrogen bonds into double chains along the *b* axis. The chains are then linked by means of further hydrogen bonds giving parallel double layers with phenyl groups pointing outwards. The layers, lying in *bc* planes, are stacked in an egg-carton fashion, by means of the phenyl groups, resulting in a close-packed arrangement.

In each molecule, the Zn atom constitutes the center of a five-coordinate $ZnNO_4$ polyhedron (Fig. 1). Two bonds are formed with the O atoms of two water molecules, while, as is usual in complexes formed by this type of ligand, there are three bonds to the doubly deprotonated L^{2-} ligand involving atoms O(2), O(4) and N(1). This tridentate behaviour results in the formation of two five-membered rings having the Zn—N(1) bond in common. The dihedral angle between the least-squares planes of these rings is 166.9 (2)°.
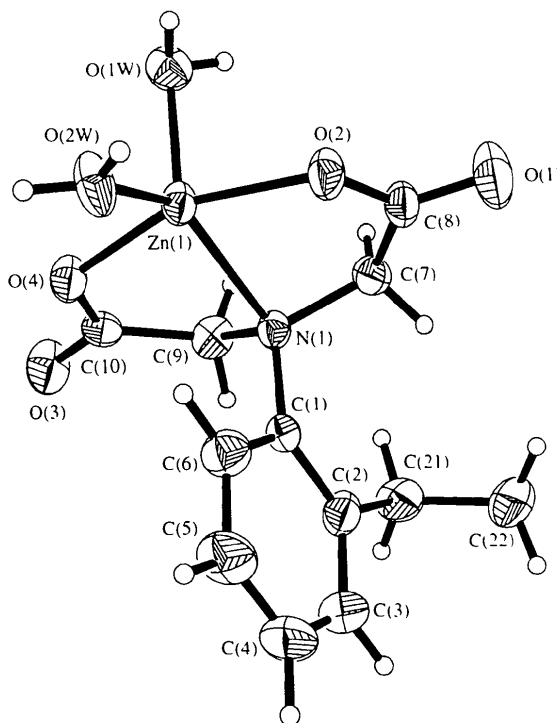

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the title molecule. Ellipsoids are drawn at the 50% probability level.

The coordination environment around the Zn atom is, therefore, made up of four short bonds of around 2.0 Å involving the four O atoms and a longer bond of 2.258 (4) Å formed with the N atom of the ligand. This geometry may be described as an intermediate member of the continuous series between square-based pyramidal and trigonal-bipyramidal geometries. The dis-

tortion can be measured using the index τ (Addison, Rao, Reedijk, Rijn & Verschoor, 1984), which is unity for perfect trigonal-bipyramidal geometry and zero for square-pyramidal geometry. The calculated value for [Zn(L)(H$_2$O)$_2$] is 0.36 and so the coordination polyhedron is best described as a square-based pyramid with a large trigonal-bipyramidal distortion. In this idealized square pyramid, the basal plane is defined by atoms N(1), O(2), O(2W) and O(4), and the apical position is occupied by the O(1W) atom. The dihedral angle between this basal plane and the planar benzene ring is 87.2(2)°. The strong trigonal distortion leads to the Zn atom being displaced by 0.475(1) Å from the basal plane towards the O(1W) axial donor. Deviations from planarity of up to 0.316(5) Å are observed for the four basal atoms.

Short non-bonding O$\cdots$O contacts (<3.0 Å) involving water molecules and O atoms of the carboxylato groups suggest intermolecular hydrogen bonding. Adjacent molecules are linked through O—H$\cdots$O interactions: O(1W)$\cdots$O(2)($-x$, $-y$, $-z$) 2.747(5), O(1W)$\cdots$O(3)($-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) 2.696(6), O(2W)$\cdots$O(3)(x, $\frac{1}{2}-y$, $z-\frac{1}{2}$) 2.661(6) and O(2W)$\cdots$O(1)(x, $y+1$, z) 2.599(6) Å.

Experimental

For the preparation of diaqua(2-ethylphenyliminodiacetato)-zinc(II), 2-ethylphenyliminodiacetic acid was synthesized by a modification of the method of Skubin, Kutepov & Valgin (1970), using 6 *N* HCl for direct precipitation of 2-ethylphenyl-glycine. The precipitate was separated from the mother liquor and Zn^{II} nitrate tetrahydrate was added to the liquor, whereupon a white precipitate immediately formed. The complex was filtered, repeatedly washed with an ethanol–water solution and dried in air. A suspension of 0.5 g (1.49 mmol) of the precipitate in 50 ml of an ethanol/water mixture (20:1) was heated to boiling, whereupon 10 ml of pyridine were added and the resulting mixture refluxed for 10 min. The solution was filtered to remove any residual solid and the filtrate was allowed to stand at room temperature. When the solvent was evaporated, well developed colorless crystals of the [Zn(L)(H$_2$O)$_2$] complex were obtained. The density D_m was measured by flotation in 1,1-dibromoethane/*cis*-1,2-dichloroethene.

Crystal data

[Zn(C$_{12}$H$_{13}$NO$_4$)(H$_2$O)$_2$]
$M_r = 336.6$
Monoclinic
$P2_1/c$
$a = 12.462(2)$ Å
$b = 7.722(2)$ Å
$c = 15.453(3)$ Å
$\beta = 110.16(3)°$
$V = 1396.0(5)$ Å^3
$Z = 4$
$D_x = 1.602$ Mg m^{-3}
$D_m = 1.616$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.5–17.5°$
$\mu = 1.783$ mm^{-1}
$T = 294$ K
Tabular
$0.20 \times 0.18 \times 0.09$ mm
Colorless

Data collection

Stoe Siemens AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.701$, $T_{max} = 0.849$
6727 measured reflections
6123 independent reflections

1798 observed reflections
[$F > 6\sigma(F)$]
$R_{int} = 0.0388$
$\theta_{max} = 32.5°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 12$
$l = -24 \rightarrow 23$
3 standard reflections
frequency: 140 min
intensity decay: 4.3%

Refinement

Refinement on F
$R = 0.0387$
$wR = 0.0420$
$S = 1.62$
1798 reflections
210 parameters
Only H-atom U's refined
Unit weights applied

$(\Delta/\sigma)_{max} = 0.417$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 55, 99 and 149)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
Zn(1)	0.1127(1)	0.1277(1)	0.1527(1)	0.027(1)
O(2W)	0.1550(5)	0.3052(5)	0.0799(3)	0.041(2)
O(4)	0.1219(3)	0.2783(5)	0.2611(2)	0.032(1)
O(2)	0.1417(4)	-0.0752(5)	0.0826(3)	0.036(1)
O(1W)	-0.0603(3)	0.1032(5)	0.1062(2)	0.035(1)
N(1)	0.2038(3)	-0.0542(5)	0.2693(3)	0.023(1)
O(3)	0.1338(4)	0.2725(5)	0.4070(3)	0.042(2)
C(10)	0.1368(4)	0.2000(7)	0.3360(3)	0.026(2)
C(1)	0.3282(4)	-0.0383(6)	0.3049(3)	0.025(2)
C(9)	0.1534(5)	0.0037(7)	0.3388(4)	0.031(2)
C(8)	0.1512(5)	-0.2219(7)	0.1220(4)	0.030(2)
C(7)	0.1635(5)	-0.2224(7)	0.2242(3)	0.029(2)
O(1)	0.1479(4)	-0.3585(6)	0.0824(3)	0.054(2)
C(2)	0.3984(5)	-0.1479(7)	0.3741(3)	0.034(2)
C(5)	0.4944(5)	0.1214(10)	0.3026(4)	0.047(2)
C(3)	0.5154(5)	-0.1166(9)	0.4048(4)	0.044(2)
C(6)	0.3778(5)	0.0940(7)	0.2704(4)	0.037(2)
C(22)	0.3871(6)	-0.4755(8)	0.3889(5)	0.053(3)
C(21)	0.3555(6)	-0.2983(8)	0.4172(4)	0.041(2)
C(4)	0.5631(6)	0.0148(9)	0.3711(5)	0.051(3)

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

Zn(1)—O(2W)	1.957(5)	C(10)—C(9)	1.528(8)
Zn(1)—O(4)	2.009(4)	C(1)—C(2)	1.407(7)
Zn(1)—O(2)	2.007(4)	C(1)—C(6)	1.391(8)
Zn(1)—O(1W)	2.033(4)	C(8)—C(7)	1.533(8)
Zn(1)—N(1)	2.258(4)	C(8)—O(1)	1.214(7)
O(4)—C(10)	1.262(6)	C(2)—C(3)	1.390(8)
O(2)—C(8)	1.272(6)	C(2)—C(21)	1.525(9)
N(1)—C(1)	1.461(6)	C(5)—C(6)	1.380(8)
N(1)—C(9)	1.488(6)	C(5)—C(4)	1.381(9)
N(1)—C(7)	1.478(6)	C(3)—C(4)	1.367(10)
O(3)—C(10)	1.244(7)	C(22)—C(21)	1.529(9)
O(2W)—Zn(1)—O(4)	97.1(2)	O(4)—C(10)—C(9)	118.5(5)
O(2W)—Zn(1)—O(2)	95.9(2)	O(3)—C(10)—C(9)	117.7(5)
O(4)—Zn(1)—O(2)	158.8(1)	N(1)—C(1)—C(2)	122.4(5)
O(2W)—Zn(1)—O(1W)	108.9(2)	N(1)—C(1)—C(6)	118.1(4)
O(4)—Zn(1)—O(1W)	95.6(2)	C(2)—C(1)—C(6)	119.4(5)
O(2)—Zn(1)—O(1W)	95.9(2)	N(1)—C(9)—C(10)	111.3(5)
O(2W)—Zn(1)—N(1)	137.2(2)	O(2)—C(8)—C(7)	117.1(5)
O(4)—Zn(1)—N(1)	80.0(1)	O(2)—C(8)—O(1)	123.4(5)
O(2)—Zn(1)—N(1)	79.1(1)	C(7)—C(8)—O(1)	119.5(5)
O(1W)—Zn(1)—N(1)	113.9(2)	N(1)—C(7)—C(8)	112.4(4)

Zn(1)—O(4)—C(10)	115.8 (3)	C(1)—C(2)—C(3)	117.3 (5)
Zn(1)—O(2)—C(8)	116.2 (4)	C(1)—C(2)—C(21)	124.8 (5)
Zn(1)—N(1)—C(1)	115.1 (3)	C(3)—C(2)—C(21)	117.9 (5)
Zn(1)—N(1)—C(9)	99.7 (3)	C(6)—C(5)—C(4)	118.8 (7)
C(1)—N(1)—C(9)	111.1 (4)	C(2)—C(3)—C(4)	122.8 (5)
Zn(1)—N(1)—C(7)	100.0 (2)	C(1)—C(6)—C(5)	121.7 (5)
C(1)—N(1)—C(7)	113.3 (4)	C(2)—C(21)—C(22)	113.2 (6)
C(9)—N(1)—C(7)	116.4 (4)	C(5)—C(4)—C(3)	119.9 (6)
O(4)—C(10)—O(3)	123.7 (5)		

Data collection: *DIF4* (Stoe & Cie, 1991*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXTL-Plus*88 (Sheldrick, 1988). Program(s) used to refine structure: *SHELXTL-Plus*88. Molecular graphics: *SHELXTL-Plus*88.

References

Addison, A. W., Rao, T. N., Reedijk, J., Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. C. (1968). *Acta Cryst.* A24, 351–359.

Sheldrick, G. M. (1988). *SHELXTL-Plus*88 *Structure Determination Software Programs.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Skubin, V. K., Kutepov, D. F. & Valgin, A. D. (1970). *Tr. Mosk. Khim. Tekhnol. Inst.* 66, 55–58.

Stoe & Cie (1991*a*). *DIF4. Diffractometer Control Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1991*b*). *REDU4. Data Reduction Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

Trimethyloxosulfonium Salts. IX. Study of some Mixed Compounds, (CH3)3SOCdCl3-xBrx

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Abstract

Crystal structures of six $(CH_3)_3SOCdCl_{3-x}Br_x$ mixed compounds [(1) $x = 2.116$, (2) $x = 1.787$, (3) $x = 1.183$, (4) $x = 0.962$, (5) $x = 0.607$, (6) $x = 0.286$]

have been determined. Each has space group *Pnma* and is a structural analogue of $(CH_3)_3SOCdCl_3$ and $(CH_3)_3SOCdBr_3$, reported previously. The distribution of Br and Cl atoms among the two anionic sites was especially studied. We have shown that the occupation probabilities are related to the x value but do not vary with it linearly: the Cl atoms showed a preference for the most symmetric site (*m* symmetry), while the Br atoms were better located on a general position more distant from the Cd ion. It is therefore not possible to describe these mixed compounds in terms of continuous solid-solution series.

Comment

In a previous paper (Puget, Jannin, de Brauer & Perret, 1991) we described the structures of the isostructural *catena*-trichlorocadmate and *catena*-tribromocadmate salts of $(CH_3)_3SO$. As a continuation, the crystal structures of six compositional analogues $(CH_3)_3SOCdCl_{3-x}Br_x$ are reported here. The precision of the results is very good and the crystal growth process leads to homogeneous bromine and chlorine composition in the whole crystal. Therefore, this study allows us to examine the influence of the site type on the kind of anionic substitution and the modifications resulting from it. No papers in the literature seem to deal with this subject for the Cl–Br couple. We have only found some reports about cationic substitution (Nord, 1983; Thomas, Mayo & Watts, 1992).

$$\text{Me} \underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{-}} SO^+Cd^{2+}[Cl_{3-x}Br_x]^{3-}$$
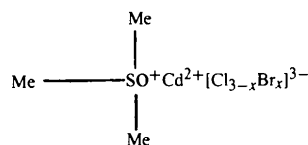
As found for the isostructural *catena*-tribromocadmate salt, the structure of each of the $(CH_3)_3SOCdCl_{3-x}Br_x$ compounds exhibits two crystallographically non-equivalent anionic sites where Br^- and Cl^- ions may both be located. The first shared (Br,Cl) site, labelled $(Br,Cl)_{(1)}$, is situated on the mirror $y = 0.25$. Its multiplicity is 4 and its occupation factor is 0.5. The second site, named $(Br,Cl)_{(2)}$, is in a general position. Its multiplicity is 8 and its total occupancy is 1. The occupation rates of Br and Cl atoms in each of the two available sites were refined with the only constraint that the total occupancy should be 0.5 on site $(Br,Cl)_{(1)}$ and 1 on site $(Br,Cl)_{(2)}$. The resulting values for each of the six compounds are listed in Table 3. Figs. 1 and 2, respectively, show the variations of the occupancies of the sites $(Br,Cl)_{(1)}$ and $(Br,Cl)_{(2)}$ *versus* the composition (x). These figures clearly show that these variations are effectively related to the composition but are not proportional to it: Br and Cl atoms are not equally