1,3-Diaminopropane as a Bridging Ligand. The Structure of μ-1,3-Diaminopropane-di(4-chlorobenzoato)zinc(II), C₁₇H₁₈N₂O₄Zn

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The structure of the title compound was determined by single-crystal X-ray methods. The compound crystallizes in the monoclinic crystal system (space group $P2_1/n$, No. 14) with $a = 6.0513(12)$, $b = 23.834(3)$, $c = 13.138(2)$ Å, $\beta = 95.871(15)°$, $V = 1885.0(6)$ Å^3 and $Z = 4$. The structure consists of di(4-chlorobenzoato)zinc(II) moieties bridged by 1,3-diaminopropane. The synperiplanar chains run diagonally along the ac-direction and are connected by hydrogen bonding mediated by the non-bonded oxygens of the 4-chlorobenzoate anions. The coordination around Zn(II) is approximately tetrahedral. The two Zn–O bond lengths are 1.951(4) and 1.946(4), and the two Zn–N bond lengths are 2.058(4) and 2.049(4) Å, respectively. Ab initio calculations performed at the STO-3G* level for the complex unit and the optimized 4-chlorobenzoate anion show that bonding to zinc increases electron density at the bonded oxygen, while the opposite happens in the non-bonded oxygen. The bond order increases in the C–O(non-bonded) bond, while the other C–O bond remains as a single bond. There are some relatively short intermolecular distances between the 4-chlorobenzoate anions.

1,3-Diaminopropane (hereafter tn) is known to form chelates readily with Cu(II), Ni(II), Co(III) and Pt(II) cations. There are only two copper(II) complexes, where tn acts as a bridge.[1,2] The most frequent conformation of a chelate ring is the chair conformation in the bis chelates.
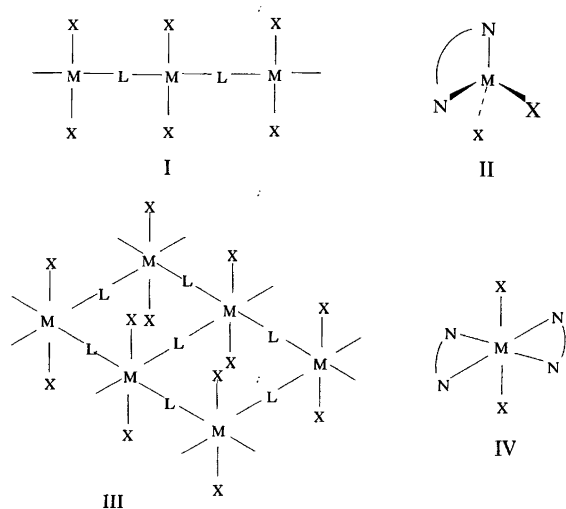
Based upon molecular conductance and IR measurements Ahuja and Singh predicted that there should be at

I

II

III

IV

Scheme 1.

least four structural types for the coordination compounds of Zn^{2+}, Cd^{2+} and Hg^{2+} (I–IV, Scheme 1).[3]

There is no ligand field stabilization effect in these ions because of their completed d-shell. The chelate effect as such is not shown to depend on ligand field stabilization. It seems that d^{10}-metal cations Zn^{2+}, Cd^{2+} and Hg^{2+} are seemingly insensitive to the chelate effect if tn (or its derivative) is used as a ligand, however. There are a number of complexes displaying bridge formation: in bis(μ-1,3-diaminopropane-N,N′)mercury(II) sulfate dihydrate (1),[4] bis(2,2-dimethylpropane-1,3-diamine)dibromocadmium(II) bis(μ-2,2-dimethylpropane-1,3-diamine)bis(2,2-dimethylpropane-1,3-diamine)tetrabromocadmium(II) (2),[5] catena[μ-1,3-diaminopropane-N,N′)-(1,3-diaminopropane-N,N′)zinc(II) dichloride][6] and catena[(μ-1,3-diaminopropane-N,N′)(1,3-diaminopropane-N,N′)-cadmium(II) iodide (3)[6] there is a bridging tn or its derivative. In bis(2,2-dimethylpropane-1,3-diaminato-N,N′,N″,N‴)(2,2-dimethylpropane-1,3-diamine-N)zinc(II) (4)[7] there are two chelate rings, but the third tn derivative is only monocoordinated.

According to potentiometric titrations, Cd(II) forms species ML, ML₂ and even ML₃.[8] There are no similar reports about complex formation for either Hg(II) or Zn(II).

In order to study further the complex formation be-

tween tn and the Zn(II) cation, a new complex was synthesized. Its structure is reported here with *ab initio* calculations for the complex unit. Additional calculations carried out for the 4-chlorobenzoate anion in gas phase gave better insight into the electronic properties.

Experimental

Materials. Pale yellow crystals were obtained by heating and stirring a mixture of a water–ethanol solution and $ZnCO_3$ (Merck. *p.a.*), 4-chlorobenzoic acid (Merck *p.a.*) and tn (Merck, *for synthesis*) in the molar ratio 1:1:2.

Crystal data. These were as follows: $C_{17}H_{18}N_2O_4Zn$, $M = 381.43$, monoclinic, $a = 6.0513(12)$, $b = 23.834(3)$, $c = 13.138(2)$ Å, $\beta = 95.871(15)°$, $V = 1885.0(6)$ Å^3 (by least-squares refinement of diffractometer angles for 18 independent well centered reflections, $\lambda = 0.710\ 69$ Å), space group $P2_1/n$, No. 14, $Z = 4$, $D_c = 1.59$, $D_m = 1.58$ g cm^{-3}, $F(000) = 920$. Pale yellow prisms. Crystal dimensions $0.18 \times 0.20 \times 0.35$ mm, $\mu = 1.61$ mm^{-1}.

Data collection and processing. A Nicolet P3 diffractometer was used in the ω-scan mode, with a variable scan speed of 2.0–20.0° min^{-1} and graphite-monochromated Mo$K\alpha$ radiation; unique reflections were measured for $3.0 \leq 2\Theta \leq 55.0$, with no absorption correction, giving 2453 independent reflections with $F > 4\sigma(F_o)$. No decay, but Lorentz and polarization corrections were made.

Structure analysis and refinement. Patterson synthesis was carried out followed by difference Fourier techniques. A full matrix least-squares refinement was made with the anisotropic and isotropic thermal parameters for the non-hydrogen and hydrogen atoms, respectively. The weighting scheme $w = 1/\sigma^2$ (with F_o from counting statistics) gave satisfactory agreement analyses. Final R- and R'-values were 0.051 and 0.034, respectively. The neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package. The calculations were carried out with SHELXS[9] and XTAL[10a] software. The figures were drawn by PLUTON[11] and ORTEP.[10b]

Ab initio *calculations.* These were carried out using the Gaussian 92 program package.[12] The properties of chemical bonding were evaluated by the NBO subprogram.[13] The basis set was STO-3G*. This basis set is the only one in the Gaussian package to allow calculations with the core and metal d-orbitals in Zn(II) complexes. Because the structure is polymeric, only the coordinates for the central Zn(II) atom, two 4-chlorobenzoates and two tn molecules adjacent to the Zn(II) atom were used as input for single-point calculation. The same basis set was also used for the optimization of 4-chlorobenzoate anion so as to allow a comparison with the coordinated anion. The calculations were run on a GRAY X-MP computer of the Finnish State Computer Centre.

Table 1. Atomic positional and isotropic displacement parameters with their standard deviations for the non-hydrogen atoms.

Atom	x/a	y/b	z/c	U_{eq}[a] or U
Zn1	0.5684(1)	0.27075(3)	0.52769(4)	0.0335(2)
N1	0.7663(7)	0.2920(2)	0.4153(3)	0.035(2)
N2	0.7649(9)	0.2538(2)	0.6602(3)	0.037(2)
C1	0.678(9)	0.2817(2)	0.3069(4)	0.038(2)
C2	0.472(1)	0.3168(2)	0.2782(4)	0.036(2)
C3	0.856(1)	0.1962(2)	0.6710(4)	0.038(2)
O1	0.4466(6)	0.1968(2)	0.4938(3)	0.051(2)
O2	0.1614(6).	0.2276(2)	0.3887(3)	0.045(1)
C4	0.2040(8)	0.1297(2)	0.4129(4)	0.032(2)
C5	0.349(1)	0.0863(3)	0.4355(5)	0.048(2)
C6	0.287(1)	0.0317(3)	0.4148(5)	0.059(3)
C7	0.070(1)	0.0197(2)	0.3769(4)	0.044(2)
C8	-0.076(1)	0.0622(3)	0.3536(5)	0.048(3)
C9	-0.012(1)	0.1178(3)	0.3702(4)	0.041(2)
C10	0.2690(9)	0.1893(2)	0.4328(4)	0.034(2)
C11	-0.0101(3)	-0.04935(6)	0.3551(1)	0.0754(8)
O11	0.4505(6)	0.3459(1)	0.5459(3)	0.045(1)
O12	0.0.1558(7)	0.3095(2)	0.6072(3)	0.059(2)
C14	0.1845(9)	0.4081(2)	0.6029(3)	0.030(2)
C15	-0.021(1)	0.4173(3)	0.6403(4)	0.044(2)
C16	-0.088(1)	0.4722(3)	0.6608(5)	0.047(2)
C17	0.046(1)	0.5164(2)	0.6455(4)	0.042(2)
C18	0.249(1)	0.5086(2)	0.6063(4)	0.044(2)
C19	0.3148(9)	0.4540(2)	0.5853(4)	0.036(2)
C20	0.265(1)	0.3500(2)	0.5839(4)	0.036(2)
C12	-0.0366(3)	0.58337(7)	0.6744(1)	0.0695(7)

$^a U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i \cdot a_j.$

Results and discussion

The final atomic coordinates are reported in Table 1. The bond lengths and angles for the non-hydrogen atoms are given in Table 2, with the atoms labelled as in Fig. 1. The structure consists of di(4-chlorobenzoato)zinc(II) moieties connected by tn. The Zn–tn–Zn chains, which run diagonally along the *ac*-direction (Fig. 2), are connected by hydrogen bonding via the amino groups to the tn molecule and the non-coordinated oxygen atoms of the carboxylate group of the benzoate anions.

The four nearest atoms around the central Zn(II) ion display distorted tetrahedral geometry. The distances from the central Zn(II) ion to the carboxylate oxygens O2 and O12 are 3.089(3) and 2.951(4) Å, which are clearly too long for bonding. Since the *d*-shell is filled, the stereochemistry of the Zn(II) cation is determined solely by size, electrostatic forces and covalent binding forces. The bond distances are expected to correlate with the coordination number, as shown in Table 3. When the coordination number increases from four to six, the average bond lengths increase.

Although the zinc(II) cation readily forms single chelate rings with 2,2-dimethylpropanediamine,[14] the propensity for bridging increases with the number of the participating ligands. An example is compound 4, where the third ligand is only monodentately coordinated. In the title compound the tn molecule prefers bridging instead of chelate formation. However, the CSD reports seven compounds containing a tris(en)Zn(II) chelate unit.

The di(4-dichlorobenzoato)zinc(II) moieties are bridged by tn molecules. The title compound belongs to category I suggested by Ahuja and Singh (Scheme 1). The tn molecule displays anticlinal conformation with the torsion angle C1–C2–C3–N2 of 64.3(7)°. In 1,3-prop-
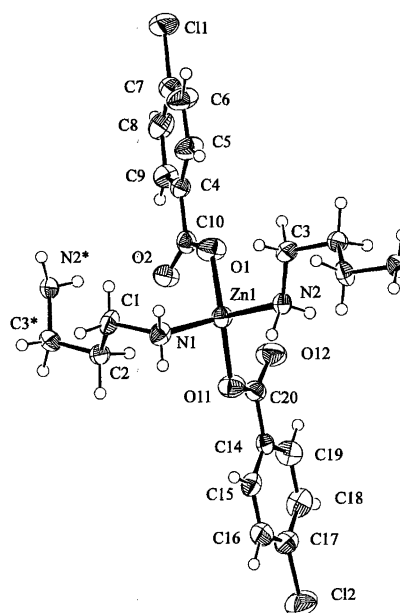

Fig. 1. An ORTEP drawing showing the labeling of the atoms. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

anediammonium tetrachlorozincate(II) the protonated tn molecule has a synperiplanar conformation with extensive hydrogen bonding between nitrogen and chlorine atoms.[15] Similar synperiplanar conformation is found in 1,3-propanediammonium chloride[16] and catena[(μ-iodo)(μ-1,3-diaminopropane-N,N')(1,3-diaminopropane-N,N')cadmium(II) iodide].[6] In catena[μ-1,3-diaminopropane-N,N')(1,3-diaminopropane-N,N')zinc(II)dichloride] there are two tn bridges, with one displaying synperiplanar conformation[6] while the other adopts the an-

Table 2. Selected bond lengths (in Å) and angles (in O) with their standard deviations for the non-hydrogen atoms.

Bond distances

Zn1–N1	2.057(5)	C2–C3	1.541(7)
Zn1–N2	2.045(5)	O1–C10	1.285(6)
Zn1–O1	1.946(4)	O2–C10	1.231(6)
Zn1–O11	1.951(3)	C4–C10	1.488(7)
N1–C1	1.490(7)	O11–C20	1.277(7)
N2–C3	1.480(7)	O12–C20	1.228(7)
C1–C2	1.514(8)	C14–C20	1.499(7)

Bond angles

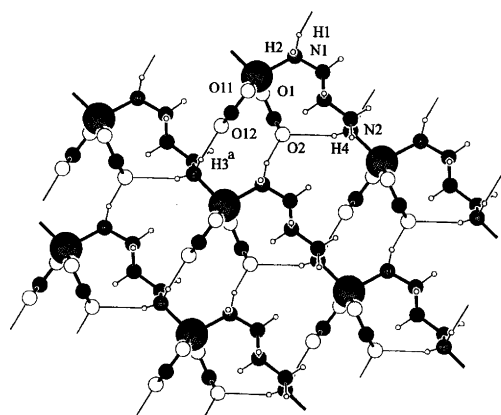|			
N1–Zn1–N2	109.2(2)	C5–C4–C9	119.0(5)
N1–Zn1–O1	107.1(2)	C5–C4–C10	122.0(5)
N1–Zn1–O11	96.3(2)	C9–C4–C10	119.0(5)
N2–Zn1–O1	100.9(2)	O1–C10–O2	123.9(5)
N2–Zn1–O11	105.4(2)	O1–C10–C4	115.6(4)
O1–Zn1–O11	136.5(2)	O2–C10–C4	120.4(4)
Zn1–N1–C1	117.9(3)	Zn1–O11–C20	117.8(3)
Zn1–N2–C3	116.3(3)	O11–C20–O12	123.6(5)
N1–C1–C2	110.7(4)	O11–C20–C14	116.8(4)
C1–C2–C3	113.8(5)	O12–C20–C14	119.5(5)
N2–C3–C2	113.9(4)		

Fig. 2. A PLUTON drawing showing the hydrogen bonding system connecting the Zn–tn–Zn chains. The aromatic rings and chlorine atoms are omitted for clarity.

ticlinal conformation. The latter contains a disordered carbon atom with somewhat anomalously long C–N and short C–C distances.

Each 4-chlorobenzoate anion is bonded to the central Zn(II) ion via one oxygen. The descriptive angles are ϑ: 1.64 and 3.06 and ς: 122.81 and 117.84°, respectively, for the two anions. Thus we may say that both of the carboxylate groups and the Zn(II) ion are approximately coplanar and display syn conformation with respect to the Zn(II) ion.[17]

The distances from the carboxylate carbons C10 and C20 to the aromatic carbons C4 and C14 are 1.488(7) and 1.499(7) Å, respectively. The corresponding value for the 4-chlorobenzoic acid is 1.491(7) Å (1.495 Å after correction caused by libration).[18] Thus there is no significant difference between the neutral acid and the coordinated anion. This is in contrast with the earlier findings, since there has been a systematic elongation in the *trans*-dibenzoatobis(tn)copper(II) complexes associated with coordination.[19–21]

The bond lengths from the carboxylate carbon to the coordinated and non-coordinated oxygen atoms, respectively, are significantly different; the bond to the non-coordinated oxygen is clearly shorter in both units. This is also contrary to the earlier findings for the respective cop-

per(II) compounds, where the values are usually almost equal, as in *trans*-di(3-iodobenzoato)bis(1,3-diaminopropane)copper(II); 1.246(5) for the coordinated and 1.254(6) Å for the non-coordinated C–O bond.[20]

The difference between the coordinated and non-coordinated oxygen atoms is also seen in the natural charges as calculated by NBO. There are – 0.590 and – 0.593 additional electrons for the coordinated oxygens and – 0.383 and – 0.376 for the non-coordinated oxygens. The corresponding values for the coordinated anion in di(1,3-diaminopropane)-3,5-diaminopropane)-3,5-dinitrobenzoatocopper(II) 3,5-dinitrobenzoate are – 0.847 and – 0.670, respectively.[21] There is also a clear difference between the bonding: 1.987 and 1.988 electrons in the C–O(coordinated) and 3.969 and 3.973 electrons for the C–O(non-coordinated). Thus the bonds may well be characterized as single and double bonds, respectively.

In the optimized 4-chlorobenzoate anion the C–O bonds are equal, as expected. There are 1.989 electrons in the bonds. Thus both bonds are essentially single bonds. The electron density at the oxygen atoms is – 0.527. Thus bonding to zinc increases slightly the electron density at the oxygen bonded to zinc, but the reverse happens at the other oxygen, where there is a clear decrease of the electron density. The oxygen bonded to zinc remains single-bonded to carbon, while the bond order increases for the other oxygen. Although hydrogen bonding must influence the electron density at the non-bonded oxygen, its contribution is negligible. This is seen from the fact that the corresponding electron density for the non-bonded oxygen in di(1,3-diaminopropane)-3,5-diaminopropane)-3,5-dinitrobenzoatocopper(II) 3,5-dinitrobenzoate is clearly higher, – 0.670.[21] This oxygen is also hydrogen-bonded.

The possible hydrogen bonds are given in Table 4. The distances found for the O2···H4–N2 moiety may be too long to indicate substantial interaction. The remaining two hydrogen bonds connect the parallel Zn–tn–Zn chains. The non-bonded oxygen atoms are thus effectively forming only one hydrogen bond to an amine group. In an earlier report, such an oxygen is reported to form even three similar hydrogen bonds.[20]

The usual van der Waals radii for an aromatic ring chlorine are 1.85 and 1.80 Å, respectively. If these values

Table 3. Bond lengths Zn–N with their average values.

	(1)	(2)	(3)	(4)	$[Zn(en)_3]^{2+\,a}$	This work
Bond length Zn–N	2.041(7)	2.011(2)	2.232(5)	2.004(8)		2.057(5)
	2.041(7)	2.015(3)	2.079(6)	2.095(6)		2.045(5)
	2.041(7)	1.992(2)	2.179(5)	2.234(8)		
	2.041(7)	2.027(2)	2.046(5)	2.264(7)		
			2.093(5)			
Average	2.041(7)	2.011(15)	2.13(6)	2.15(9)	2.204(3)	2.051(6)
Coordination number	4	4	5	5	6	4

*a*Average value calculated for seven structures retrieved from Cambridge Structural Database.

Table 4. Possible hydrogen bonds in the title compound. The superscript denotes the symmetry operator given below.

	O···H/Å	O···H–N/°	O···N/Å
O2···H1^a–N1^a	1.79(7)	164(5)	2.894(6)
O2···H4–N2	2.37(5)	159(5)	3.160(6)
O12···H3^a–N2^a	1.88(8)	146(6)	2.861(7)

^{a} $-1/2+x$, $1/2-y$, $1/2+z$.

Table 5. Short distances between the 4-chlorobenzoate anions; the superscripts denote the symmetry operators given below.

Atoms	Distance/Å	Atoms	Distance/Å
C6^a···C6^b	3.574(9)	C6^a···C11^c	3.627(7)
C6^a···C16^d	3.499(9)	C7^a···C7^c	3.555(8)
C7^a···C11^c	3.646(6)	C7^a···C16^d	3.686(9)
C8^a···C14	3.532(8)	C8^a···C19	3.541(8)
C11^a···C18	3.574(6)	C16^a···C18^c	3.575(8)
C16^a···C19^c	3.676(8)	C17^a···C18^c	3.646(8)
C17^a···C19^c	3.621(7)	C12^a···C14^c	3.668(5)

^{a} $1/2+x$, $1/2-y$, $1/2+z$. ^{b} $1/2-x$, $-1/2+y$, $1/2-z$.
^{c} $-1/2-x$, $-1/2+y$, $1/2-z$. ^{d} $1+x$, y, z.

are applied as delimiters, there are a relatively large number of short intermolecular distances, as shown in Table 5. The values for the carbon–chlorine distances are similar to those reported for *trans*-di(4-chlorobenzoato)-bis(1,3-diaminopropane)copper(II) and *trans*-di(3-chlorobenzoato)bis(1,3-diaminopropane)copper(II) (shortest value 3.64 and 3.61 Å, respectively).[22] The shortest intermolecular carbon–carbon distances in the title compound seem to be shorter than in these compounds (the shortest values are 3.72 and 3.064 Å, respectively), and also shorter than in *trans*-di(3-iodobenzoato)bis(1,3-diaminopropane)copper(II).[20] It is noteworthy that the electron density at the chlorine atoms is slightly diminished in the solid state if compared with the value obtained for the anion alone in the gas phase. The reverse happens in the neighbouring carbon atom.

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