

Bis(piperidinium) *trans*-dichlorobis(3,5-dinitrobenzoato)zincate(II)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.032

wR factor = 0.084

Data-to-parameter ratio = 7.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Complexes of 3d transition metal chlorides with dinitrobenzoic acids (DNBH) and secondary amines have been synthesized in order to model processes of chemisorption of organic salts by metal surfaces. A series of compounds of composition $(\text{AmH})_2[\text{MCl}_2(\text{DNB})_2]$ (where $M = \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}$; AmH^+ is the cation of piperidine $\text{PipH}^+ = \text{C}_5\text{H}_{10}\text{NH}_2^+$ or diethylamine $\text{DaH}^+ = \text{C}_4\text{H}_{10}\text{NH}_2^+$) have been prepared, the structure of the piperidinium salt of the $\text{Zn}/3,5\text{-DNB}$ complex anion being authenticated by X-ray crystallography. In the title compound, $(\text{C}_5\text{H}_{12}\text{N})_2[\text{ZnCl}_2(\text{C}_7\text{H}_3\text{N}_2\text{O}_6)_2]$, the Zn atom is four-coordinated. The DNB ligand behaves as a monodentate ligand *via* an O atom of the carboxylate group, the other carboxylate O atom being hydrogen bonded to one of the ammonium H atoms. The other ammonium H atom of the two cations links to the coordinated chlorides, one within the complex and the other across an inversion center, so forming a dimer.

Comment

Salts formed between dinitrobenzoic acids and various secondary amines have found application as 'volatile corrosion inhibitors' due to their property of dissociation to give volatile components which can be transported through the vapor phase to deposit on metal surfaces. The deposited material then serves to protect the metal surface, though it remains unclear as to what chemical reactions may be involved in this passivation process. One possibility is that the acid component reacts with the metal to produce a surface layer of metal dinitrobenzoate and, for this reason, we have been interested in determining the structures of these seemingly simple materials. Although the carboxylate unit is perhaps the obvious site of metal ion coordination, aromatic nitro groups are well known to function as Lewis base sites, and there is some evidence from studies of corrosion inhibition by both benzoates and nitrobenzoates that either (and perhaps both) site(s) may be involved, depending on the metal.

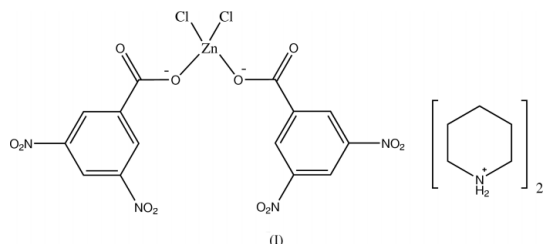
We have conducted a synthetic and structural study of the species formed by the reaction of simple metal salts with various dialkylammonium dinitrobenzoates: piperidinium (PipH^+) 3,5-dinitrobenzoate (DNB^-), piperidinium 2,4-dinitrobenzoate, and diethylammonium (DaH^+) 2,4-dinitrobenzoate. Earlier studies showed that equimolar aqueous solutions of metal salts and DNB produce compounds $\text{M}(\text{DNB})_2 \cdot n\text{H}_2\text{O}$ ($n = 2-4$) (Adeishvili, 2002), neither inorganic residue (Cl , SO_4 , NO_3) being involved in compound formation. Equimolar solutions of divalent metal acetates with DNB form compounds of the form $\text{M}(\text{DNB})_2(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ ($n = 2-4$), where acetate and DNB are monodentate ligands (Shvelashvili *et al.*, 2001). Reaction of these

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compounds in an aprotic solvent (DMSO) with molar ratio 1:2 yields $M(\text{DNB})_2(\text{DMSO})_2 \cdot n\text{H}_2\text{O}$ ($n = 2-4$), where the acetate ion, DNB^- and DMSO are all monodentate in the complex (Miminoshvili *et al.*, 2003). During the interaction of metal chlorides with organic salts with molar ratio 1:2 in a solution of a mixture of ethanol and methanol, we obtained compounds of the composition $(\text{AmH})_2[\text{MCl}_2(\text{DNB})_2]$ ($M = \text{Zn}^{\text{II}}$, Cu^{II} ; AmH^+ being the cation of piperidine PipH^+ or diethylamine DaH^+). We contend that during the synthesis in metal chloride two of the $\text{Zn}-\text{Cl}$ bonds are broken and replaced by two monodentate ligands (DNB), forming an ionic complex, with, in the case of metal chloride hydrates, two coordinated water molecules being replaced by the monodentate ligands.



The nature of the product $(\text{PipH})_2[\text{ZnCl}_2(3,5\text{-DNB})_2]$ was established by an X-ray structure determination and is shown in Fig. 1. It consists of a complex anion $[\text{ZnCl}_2(3,5\text{-DNB})_2]^{2-}$ and two PipH^+ cations. The 3,5-DNB anions are involved in the coordination sphere of the Zn atom, acting as monodentate carboxylate ligands related to each other by a pseudo- C_2 symmetry, with a weighted r.m.s. deviation of 0.361 Å (*SHELXTL*; Bruker, 1997) for all non-H atoms of the complex anion. The coordination polyhedron around the Zn atom is a distorted tetrahedron, with distances $\text{Zn}-\text{O}$ 1.950 (3) and 1.963 (2) Å, $\text{Zn}-\text{Cl}$ 2.255 (1) and 2.257 (1) Å, and angles $\text{O}-\text{Zn}-\text{O}$ 95.4 (1)°, $\text{Cl}-\text{Zn}-\text{Cl}$ 113.26 (5)°, with $\text{O}-\text{Zn}-\text{Cl}$ in the range 111.18 (9)–112.25 (9)°. These geometries can be compared with corresponding data found, for example, in dichlorobis(piperidinium-3-carboxylato- κO)-

zinc(II) (Inomata *et al.*, 2001) [$\text{Zn}-\text{O}$ 1.949 (3) and 1.957 (3) Å, $\text{Zn}-\text{Cl}$ 2.219 (1) and 2.255 (1) Å, and angles $\text{O}-\text{Zn}-\text{O}$ 98.0 (1)°, $\text{Cl}-\text{Zn}-\text{Cl}$ 113.65 (7)°, with $\text{O}-\text{Zn}-\text{Cl}$ in the range 106.8 (1)–114.4 (1)°].

The geometries of the 3,5-DNB ligands correspond to normal values and are in good agreement with parameters found earlier (Shvelashvili *et al.*, 2001; Miminoshvili *et al.*, 2003). They have an almost planar configuration and their positions relative to the Zn atom can be described by the torsion angles $\text{Zn}-\text{O}71\text{A}-\text{C}7\text{A}-\text{C}1\text{A}$ -177.0 (2)° and $\text{C}1\text{B}-\text{C}7\text{B}-\text{O}71\text{B}-\text{Zn}$ -176.8 (2)°. The dihedral angles between the carboxylate groups and the benzene rings are 6.1 (7) and 17.4 (5)° in the *A* and *B* dinitrobenzoate moieties. The dihedral angles between the nitro groups and the benzene rings vary from 2.1 (6) to 16.3 (8)°. Both cations have chair conformations and are linked to the anion by hydrogen bonds (Table 1), forming centrosymmetric dimer clusters in the crystal.

The structure of bis(piperidinium) dichlorobis(3,5-dinitrobenzoato)zincate(II) presented here is thus consistent with our assumptions relating to the character of interactions of dinitrobenzoic acids with the surface of metals during passivation processes (see above).

Experimental

A typical procedure was the following: ZnCl_2 (0.68 g, 0.5 mmol) was dissolved and heated in ethanol (10 ml) and 3,5-DNB (2.92 g, 1.4 mmol) in methanol (10 ml) was added, producing a precipitate. A slurry, formed as a result of the mixing of the solutions, was filtered and the mother liquor left for crystallization. A similar regime was applied for other $(\text{AmH})_2[\text{MCl}_2(\text{DNB})_2]$ compounds, where $M = \text{Zn}^{\text{II}}$ or Cu^{II} . Analytical data for the synthesized compounds are: (I) $\text{CuCl}_2(3,5\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{C}_5\text{H}_{12}\text{N})_2$ (deep-blue, m.p. 593 K). Analysis found: Cu 9.04, C 39.31, H 3.84, N 11.26, Cl 9.21%; calculated: Cu 8.71, C 39.54, H 4.15, N 11.53, Cl 9.72%. (II) $\text{CuCl}_2(2,4\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{C}_5\text{H}_{12}\text{N})_2$ (aquamarine, m.p. 563 K). Analysis found: Cu 9.15, C 39.68, H 3.92, N 11.15, Cl 9.35; calculated: Cu 8.71, C 39.54, H 4.15, N 11.53, Cl 9.72%. (III) $\text{CuCl}_2(2,4\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{C}_4\text{H}_{12}\text{N})_2$ (aquamarine, m.p. 423 K). Analysis found: Cu 9.54, C 38.12, H 4.13, N 11.40, Cl 10.48; calculated: Cu 9.01, C 37.48, H 4.29, N 11.92, Cl 10.05%. (IV) $\text{ZnCl}_2(3,5\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{C}_5\text{H}_{12}\text{N})_2$ (yellow, m.p. 463 K). Analysis found: Zn 8.60, C 38.98, H 3.75, N 12.05, Cl 9.15; calculated: Zn 8.94, C 39.44, H 4.14, N 11.50, Cl 9.70%. (V) $\text{ZnCl}_2(2,4\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{C}_5\text{H}_{12}\text{N})_2$ (brown, m.p. 473 K). Analysis found: Zn 9.24, C 38.94, H 3.86, N 11.61, Cl 9.34; calculated: Zn 8.94, C 39.44, H 4.14, N 11.50, Cl 9.70%. (VI) $\text{ZnCl}_2(2,4\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{C}_4\text{H}_{12}\text{N})_2$ (light yellow, m.p. 443 K). Analysis found: Zn 9.43, C 37.28, H 4.71, N 11.56, Cl 9.56; calculated: Zn 9.25, C 37.38, H 4.28, N 11.89, Cl 10.03%.

Crystal data

$(\text{C}_5\text{H}_{12}\text{N})_2[\text{ZnCl}_2(\text{C}_7\text{H}_3\text{N}_2\text{O}_6)_2]$
 $M_r = 730.81$
 Triclinic, $P\bar{1}$
 $a = 9.786$ (3) Å
 $b = 10.550$ (4) Å
 $c = 15.603$ (5) Å
 $\alpha = 97.04$ (2)°
 $\beta = 91.47$ (2)°
 $\gamma = 94.66$ (2)°
 $V = 1592.4$ (9) Å³

$Z = 2$
 $D_x = 1.524$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 12 reflections
 $\theta = 12.2\text{--}14.8^\circ$
 $\mu = 1.01$ mm⁻¹
 $T = 293$ (2) K
 Prism, pale yellow
 $0.20 \times 0.18 \times 0.10$ mm

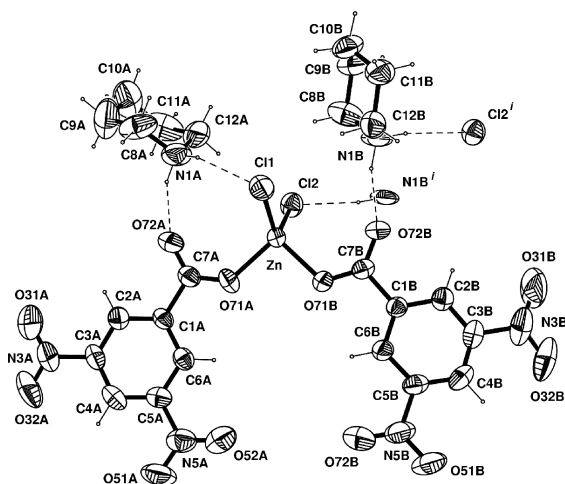


Figure 1
 Details of the hydrogen bonding in the crystal structure of (I); displacement ellipsoids of non-H atoms are drawn at the 50% probability level. [Symmetry code: (i) $-x, 1 - y, -z$.]

Data collection

Nicolet P3 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (XEMP; Nicolet, 1985)
 $T_{\min} = 0.824$, $T_{\max} = 0.906$
 3096 measured reflections
 3096 independent reflections
 3096 reflections with $I > 3\sigma(I)$

$\theta_{\max} = 22.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = 0 \rightarrow 16$
 3 standard reflections
 every 100 reflections
 intensity decay: 2.5%

Refinement

Refinement on F^2
 $R[F^2 > 3\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.04$
 3096 reflections
 407 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 1.2282P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXTL
 Extinction coefficient: 0.0011 (7)

Table 1

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H1AB \cdots O72A$	0.90	1.95	2.799 (5)	157
$N1A-H1AA \cdots Cl1$	0.90	2.33	3.189 (4)	159
$N1B-H1BA \cdots O72B$	0.90	1.86	2.734 (4)	163
$N1B-H1BB \cdots Cl2$	0.90	2.44	3.313 (4)	164

Symmetry code: (i) $-x, 1-y, -z$.

The H atoms were included using a riding model and were constrained to have $C-H(\text{aromatic}) = 0.93 \text{ \AA}$, $CH_2 = 0.97 \text{ \AA}$ and $N-H = 0.90 \text{ \AA}$, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent C or N atom.

Data collection: P3 Diffractometer Control Software (Nicolet, 1985); cell refinement: P3 Diffractometer Control Software; data reduction: PROFIT (Streltsov & Zavodnik, 1989); program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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