Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Trichloro(sarcosinio)zinc(II) monohydrate

R. V. Krishnakumar,[a] M. Subha Nandhini[b] and S. Natarajan[b]*

[a]Department of Physics, Thiagarajar College, Madurai 625 009, India, and [b]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: xray@mrna.tn.nic.in

Received 3 April 2001
Accepted 4 April 2001
Online 12 April 2001

In the title compound, $[ZnCl_3(C_3H_8NO_2)]\cdot H_2O$, the sarcosine ligand unexpectedly coordinates to the metal in the cationic form (CH_3–NH_2^+–CH_2–COOH). The Zn atom is found to have tetrahedral coordination. A head-to-tail N—H···O hydrogen bond between the screw-related molecules is present. The water molecule does not participate in metal coordination, but co-operates in the packing as a donor and acceptor in hydrogen bonds to a carboxyl O atom and as a donor to a Cl atom.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.017
wR factor = 0.053
Data-to-parameter ratio = 9.2

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

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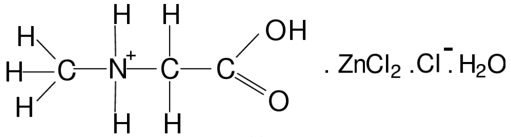
Comment

Sarcosine (*N*-methylglycine, $CH_3NH_2^+CH_2COO^-$), an α-amino acid present in several biologically important compounds, forms a number of addition compounds with inorganic acids and salts besides forming metallic complexes. The crystal structure of sarcosine itself was determined earlier in our laboratory (Mostad & Natarajan, 1989). The present study reports the crystal structure of a complex of sarcosine with $ZnCl_2$, namely trichloro(sarcosinio)zinc(II) monohydrate, (I).



(I)

The sarcosine molecule exists in the cationic form with a positively charged amino group and a protonated carboxylic acid group. In the cases of complexes with metallic salts, the amino acid normally remains as a zwitterion. The formation of the zinc complex observed in the crystals may be justified by a complex series of hydrolytic equilibria involving the solvent water molecules, the Cl^- ions and the sarcosine zwitterion. In the three other crystal structures of amino acid complexes with $ZnCl_2$ known so far, amino acid molecules exist as zwitterions in glycine with $ZnCl_2$ (Hariharan *et al.*, 1989) and L-proline with $ZnCl_2$ (Yukawa *et al.*, 1985) and adopts a cationic form in L-histidine with $ZnCl_2$ (Foster *et al.*, 1993).

In Fig. 1, the molecular structure and the atom-numbering scheme adopted is shown. The molecular main chain deviates from planarity, the C3—N1—C2—C1 torsion angle (Table 1) indicating that the C3—N1 bond is synclinal to C2—C1. Similar observations have been made in the structures of sarcosine cadmium chloride (Krishnakumar *et al*, 1996), sarcosine telluric acid adduct (Averbuch-Pouchot, 1988) and sarcosinium tartrate (Krishnakumar *et al.*, 2001). C3—N1 is antiperiplanar to C2—C1 in the crystal structure of sarcosine

DOI: 101107/S160053680100592X

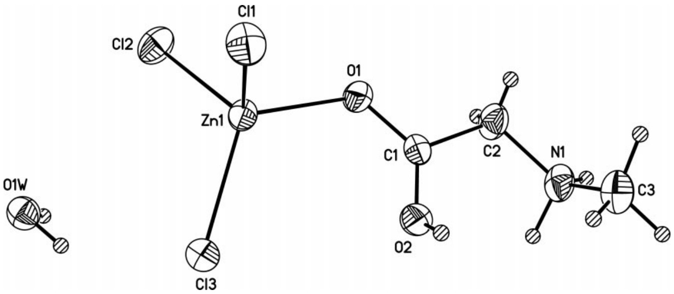


Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids.

(Mostad & Natarajan, 1989), sarcosine barium chloride (Krishnakumar & Natarajan, 1995), sarcosine sucrose (Krishnakumar & Natarajan, 1996), sarcosine oxalic acid monohydrate (Krishnakumar *et al.*, 1999) and diaquabis(sarcosinato)copper(II) (Krishnakumar *et al.*, 1994). The value of the O1—C1—O2—H1 torsion angle is −85.6°. This unusual value may be justified by the fact that the position of the hydrogen (H1) is determined by the two hydrogen bonds O2—H1···O1W^{i} (intermolecular) and N1—H1*B*···O2 (intramolecular), in which O2 is involved [symmetry code: (i) *x* + 1, *y*, *z*]. It is important to notice that both these hydrogen bonds justify the cationic status of the coordinating amino-acid ligand (see Table 2). It is interesting to notice also that the C1—O1 bond distance is remarkably longer than C1—O2 (Δ/σ = 10.25) (see Table 1), when usually in carboxylic acids, the contrary is observed [Csp^2═O = 1.214 (19) Å and Csp^2—OH = 1.308 (19) Å; Allen *et al.*, 1987] and is justified by the coordination of O1 to metal and the hydrogen bond O2 forms with the water molecule.

Zinc is known to have both tetrahedral and octahedral coordination in crystal structures (Cingi *et al.*, 1972). Zinc in the present structure has a tetrahedral coordination with three chlorines and a carboxyl O atom of the amino acid taking part. The angles around the Zn atom range from 104.2 (1) to 115.4 (1)°. Fig. 2 shows the packing of the molecules viewed down the *b* axis. A head-to-tail N—H···O hydrogen bond between the screw-related molecules is present. One of the three chlorines participates in a C—H···Cl hydrogen bond (see Table 2). The N1—H1*A*···O1^{ii} and N1—H1*B*···Cl^{iii} hydrogen bonds form a ring of $R_4^4(12)$ graph-set motif (Etter *et al.*, 1990), while the O2—H1···O1W^{i} and O1*W*—H2*W*···Cl3 interactions form a $C_2^2(8)$ chain running along [100] [symmetry codes: (ii) 2 − *x*, *y* − $\frac{1}{2}$, −*z*; (iii) *x*, *y* − 1, *z*].

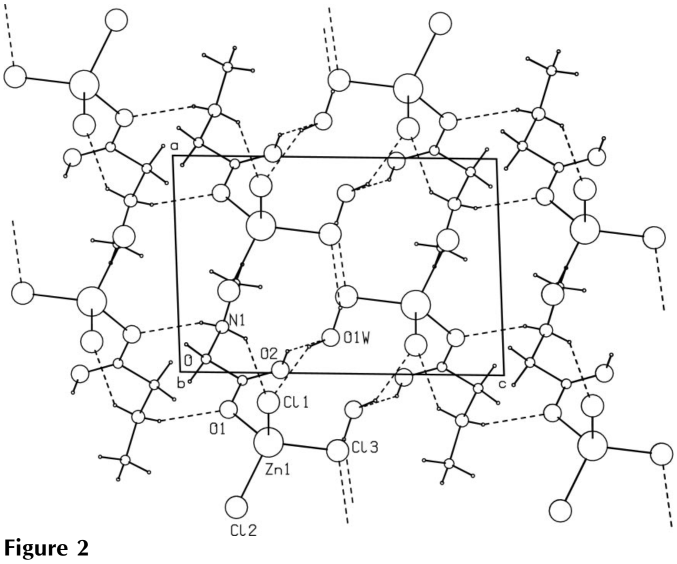


Figure 2
Packing diagram of the molecules of (I) in the unit cell viewed down the *b* axis.

Experimental

Colourless single crystals of the title complex were grown as transparent needles from a saturated aqueous solution containing sarcosine and zinc chloride in a stoichiometric ratio.

Crystal data

$[ZnCl_3(C_3H_8NO_2)]\cdot H_2O$
M_r = 279.84
Monoclinic, $P2_1$
a = 6.6181 (12) Å
b = 7.4989 (11) Å
c = 9.900 (4) Å
β = 92.62 (2)°
V = 490.8 (2) Å^3
Z = 2
D_x = 1.894 Mg m^{-3}
D_m = 1.90 (3) Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
Mo *K*α radiation
Cell parameters from 1017 reflections
θ = 6–15°
μ = 3.28 mm^{-1}
T = 293 (2) K
Plate, colourless
0.38 × 0.24 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.812, $T_{\max}$ = 0.993
1017 measured reflections
933 independent reflections
913 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.008
$\theta_{\max}$ = 25.0°
h = 0 → 7
k = 0 → 8
l = −11 → 11
2 standard reflections every 200 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.053
S = 1.28
933 reflections
101 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.1562P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.30 e Å^{-3}
$\Delta\rho_{\min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.051 (4)
Absolute structure: Flack (1983)
Flack parameter = 0.010 (18)

Table 1
Selected geometric parameters (Å, °).

O1—Zn1—Cl2	106.53 (10)	C2—N1—C3	116.3 (4)
O1—Zn1—Cl3	115.41 (10)	O2—C1—O1	126.5 (4)
Cl2—Zn1—Cl3	111.58 (5)	O2—C1—C2	120.2 (4)
O1—Zn1—Cl1	104.18 (10)	O1—C1—C2	113.3 (4)
Cl2—Zn1—Cl1	108.82 (5)	N1—C2—C1	113.2 (4)
Cl3—Zn1—Cl1	109.91 (5)		
C3—N1—C2—C1	−77.7 (5)	O1—C1—C2—N1	−177.5 (4)
O2—C1—C2—N1	1.4 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···O1*W*$^{\rm i}$	0.82	2.21	2.919 (5)	144
N1—H1*A*···O1$^{\rm ii}$	0.90	2.21	3.001 (5)	146
N1—H1*B*···O2	0.90	2.48	2.726 (5)	96
N1—H1*B*···Cl1$^{\rm iii}$	0.90	2.46	3.224 (4)	142
O1*W*—H1*W*···O2$^{\rm iv}$	0.85	2.45	2.943 (5)	118
O1*W*—H1*W*···Cl1$^{\rm v}$	0.85	2.54	3.220 (4)	138
O1*W*—H2*W*···Cl3$^{\rm iv}$	0.86	2.39	3.246 (4)	173
C2—H2*A*···Cl2$^{\rm vi}$	0.97	2.82	3.702 (5)	152

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

H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms using *SHELXL*97 (Sheldrick, 1997) defaults. The positions of the water H atoms were calculated using *HYDROGEN* (Nardelli, 1999), with O—H = 0.85 Å, H—O—H = 107° and $U(\mathrm{H})_{\mathrm{eq}} = 1.2U_{\mathrm{eq}}$ of the parent atoms, and were not included in the refinement.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

The authors thank the Council of Scientific and Industrial Research (CSIR), India, for financial assistance. The authors also thank the UGC for the DRS programme and the Bioinformatics Centre, Madurai Kamaraj University, for providing access to the Cambridge Structural Database (Allen & Kennard, 1993).

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