# Anhydrous polymeric zinc(II) heptanoate

Jérôme Peultier, Michel Francois and Jean Steinmetz

*Laboratoire de Chimie Minérale, UMR 7555, Université Henri Poincaré, Nancy I, Faculté des Sciences, BP 239, 54506 Vandoeuvre lés Nancy CEDEX, France. E-mail: francois@lcm.u-nancy.fr*

## Abstract

The structure of the title compound, poly[zinc(II)-bis($\mu$-heptanoato-$O:O'$)], $[Zn(C_7H_{13}O_2)_2]_n$, consists of polymeric sheets parallel to (001) in which tetrahedrally coordinated $Zn^{2+}$ cations are connected by carboxylate bridges in a *syn–anti* arrangement.

## Comment

The structure analysis of the title compound, (I), was undertaken in order to provide information about the nature of the metallic soap protecting metallic zinc surfaces, the corrosion of which is inhibited by addition of a saturated linear sodium carboxylate in the aqueous medium.

(I)
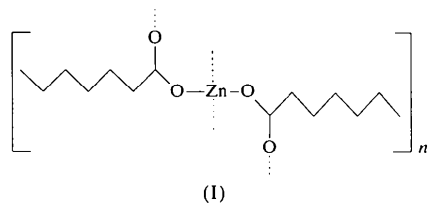
As shown in Fig. 1, the structure of (I) consists of polymeric two-dimensional sheets parallel to (001). The tetrahedrally coordinated Zn atoms are connected by *syn–anti* heptanoate bridges. Each sheet is characterized by an internal plane containing $Zn^{2+}$ cations, surrounded by tetrahedra of $O^{2-}$ anions, whereas the alkyl chains protrude from each side of this plane. The environment of the $Zn^{2+}$ cations is shown in Fig. 2. The four $O^{2-}$ anions belong to four different carboxylate chains. The two linear carboxylate chains formed by C1n ($n = 1–7$) atoms are parallel, while an angle of about 62 (1)° exists between the two carboxylate chains formed by C2n atoms. The same arrangement is observed in other known linear carboxylates, with an angle of 62 (1)° in butanoate (Blair *et al.*, 1993), 64 (2)° in propionate (Clegg *et al.*, 1986; Goldschmied *et al.*, 1977) and 69 (2)° in acetate (Clegg *et al.*, 1987; Frada, 1992). So, orientation of two of the four linear carboxylate chains surrounding the $Zn^{2+}$ cation is only slightly dependent on their length. Consequently, the connection between the tetrahedral units will be approximately the same

within the sheets. The differences observed as a function of the linear chain length lead, of course, to different thicknesses of the sheets, but, more interestingly, to various space groups in the $Zn(C_nH_{2n-1}O_2)_2$ carboxylate series: $n = 2$ ($P2_1/c$ or $C2/c$), $n = 3$ ($P2_1/c$ or $Pna2_1$) and $n = 4$ ($P2_1/c$). It is clear that the various ways of stacking the sheets, between which there is no covalent bonding, only van der Waals interactions, are responsible for the symmetry changes. It is worth noting that an anhydrous $Zn^{II}$ acetate modification with a strongly three-dimensional character had been found previously (Capilla & Aranda, 1979).
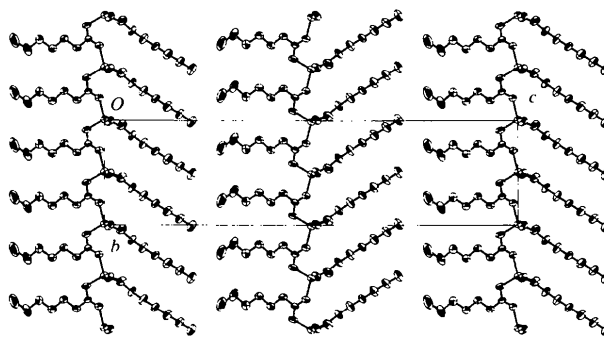


Fig. 1. Projection of the title structure along [100]. Displacement ellipsoids are drawn at the 70% probability level (*ATOMS*; Dowty, 1995). H atoms have been omitted for clarity.
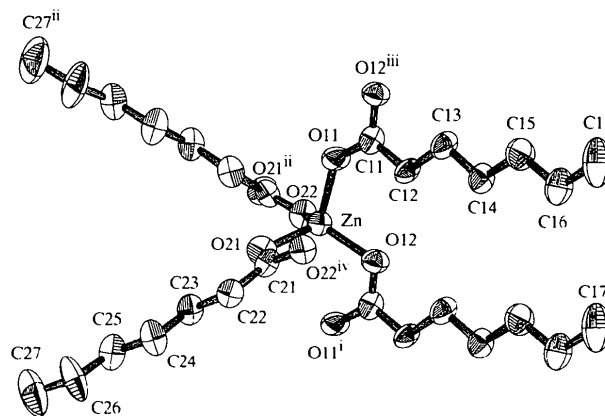


Fig. 2. The tetrahedral $Zn^{II}$ environment showing the orientation of the linear heptanoate chains. Displacement ellipsoids are drawn at the 70% probability level (*ATOMS*; Dowty, 1995). The symmetry codes are as in Table 1.

## Experimental

The title compound was prepared by reaction of a weakly acidic (pH 5.5) solution of zinc nitrate with sodium heptanoate. The precipitates obtained were washed with distilled water and dried. A small quantity of the product was recrystallized from ethanol for one month at room temperature. Colorless crystals appeared as small plates with well developed (001) faces.

*Crystal data*

[Zn(C$_7$H$_{13}$O$_2$)$_2$]
$M_r$ = 323.72
Orthorhombic
$Pbc2_1$
$a$ = 4.7651 (6) Å
$b$ = 9.3404 (15) Å
$c$ = 37.066 (6) Å
$V$ = 1649.7 (4) Å$^3$
$Z$ = 4
$D_x$ = 1.303 Mg m$^{-3}$
$D_m$ not measured

Cu $K\alpha$ radiation
$\lambda$ = 1.5418 Å
Cell parameters from 25
    reflections
$\theta$ = 20–40°
$\mu$ = 2.129 mm$^{-1}$
$T$ = 293 (2) K
Plate
0.175 × 0.135 × 0.004 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4
    diffractometer
$\omega/2\theta$ scans
Absorption correction:
    $\psi$ scan fitted by spherical
    harmonic functions
    (*SORTAV*; Blessing, 1995)
    $T_{min}$ = 0.76, $T_{max}$ = 0.99
4714 measured reflections
1582 independent reflections

847 reflections with
    $I > 2\sigma(I)$
$R_{int}$ = 0.063
$\theta_{max}$ = 69.81°
$h$ = 0 → 5
$k$ = 0 → 11
$l$ = 0 → 44
3 standard reflections
    frequency: 180 min
    intensity decay: 3.8%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.159
$S$ = 0.908
1582 reflections
173 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.502 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.536 e Å$^{-3}$
Extinction correction:
    *SHELXL*97
Extinction coefficient:
    0.0026 (4)
Scattering factors from
    *International Tables for*
    *Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| Zn1—O12 | 1.920 (11) | O12—C11$^i$ | 1.282 (16) |
|---|---|---|---|
| Zn1—O11 | 1.946 (8) | O21—C21 | 1.257 (12) |
| Zn1—O21 | 1.975 (11) | O22—C21$^{ii}$ | 1.245 (14) |
| Zn1—O22 | 1.976 (6) | C11—O12$^{iii}$ | 1.282 (16) |
| O11—C11 | 1.274 (14) | C21—O22$^{iv}$ | 1.245 (14) |
| | | | |
| O12—Zn1—O11 | 107.0 (4) | C21—O21—Zn1 | 113.8 (9) |
| O12—Zn1—O21 | 112.7 (3) | C21$^{ii}$—O22—Zn1 | 128.0 (7) |
| O11—Zn1—O21 | 117.2 (4) | O11—C11—O12$^{iii}$ | 120.1 (12) |
| O12—Zn1—O22 | 114.6 (4) | O11—C11—C12 | 120.5 (12) |
| O11—Zn1—O22 | 100.1 (3) | O12$^{iii}$—C11—C12 | 119.1 (12) |
| O21—Zn1—O22 | 104.8 (3) | O22$^{iv}$—C21—O21 | 120.5 (11) |
| C11—O11—Zn1 | 133.0 (8) | O22$^{iv}$—C21—C22 | 120.4 (9) |
| C11$^i$—O12—Zn1 | 118.4 (9) | O21—C21—C22 | 119.1 (11) |

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREAR*97 (Blessing, 1987). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *WINWORD* (Version 5.0).

The authors are grateful to the Services Communs de Diffractométrie Automatique of the University Henri Poincaré.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1286). Services for accessing these data are described at the back of the journal.

### References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Blair, J., Howie, R. A. & Wardell, J. L. (1993). *Acta Cryst.* C49, 219–221.
Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
Blessing, R. H. (1995). *Acta Cryst.* A51, 33–38.
Capilla, A. V. & Aranda, R. A. (1979). *Cryst. Struct. Commun.* **8**, 795–799.
Clegg, W., Little, I. R. & Straughan, B. R. (1986). *Acta Cryst.* C42, 1701–1703.
Clegg, W., Little, I. R. & Straughan, B. R. (1987). *Acta Cryst.* C43, 456–457.
Dowty, E. (1995). *ATOMS for Windows*. Version 3.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frada, J. M. (1992). Thesis (No. 92/NAN1/0408), Université Henri Poincaré, Nancy, France.
Goldschmied, E., Rae, A. D. & Stephenson. N. C. (1977). *Acta Cryst.* B33, 2117–2120.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

# [Co(phen)(thiourea)(H$_2$O)Cl$_2$]·thiourea (phen is 1,10-phenanthroline)

Leopoldo Suescun, Raúl A. Mariezcurrena and Alvaro W. Mombrú

*Laboratorio de Cristalografía y Química del Estado Sólido, Facultad de Química, Universidad de la República, Av. Gral Flores 2124, Casilla de Correos 1157, Montevideo, Uruguay. E-mail: leopoldo@bilbo.edu.uy*

## Abstract

The structure of aquadichloro(1,10-phenanthroline)-(thiourea-*S*)cobalt(II)–thiourea (1/1), [CoCl$_2$(C$_{12}$H$_8$N$_2$)-(CH$_4$N$_2$S)(H$_2$O)]·CH$_4$N$_2$S, is formed by the neutral cobalt(II) complex and a thiourea molecule. High-spin Co$^{II}$ is present in the structure as can be deduced from the Co—N bond distances. The packing of the structure is directed by hydrogen bonds which stabilize the presence of both thiourea molecules.

## Comment

The change in the electronic configuration of Co$^{II}$ cations from high- to low-spin states has been studied