Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Phenanthroline complexes of zinc and calcium carbamates

**Günter Reck* and Roland Becker**

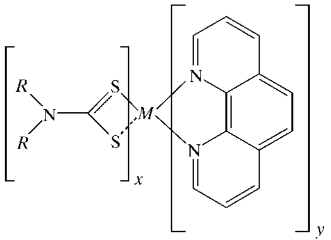
Bundesanstalt für Materialforschung und -prüfung, Richard-Willstätter-Straße 11, D-12489 Berlin, Germany
Correspondence e-mail: guenter.reck@bam.de

Received 5 January 2004
Accepted 20 January 2004
Online 19 February 2004

Bis(*N*,*N*-di-*n*-butyldithiocarbamato-$\kappa^2S,S'$)(1,10-phenanthroline-$\kappa^2N,N'$)zinc(II) ethanol hemisolvate, $[\mathrm{Zn}(\mathrm{C_9H_{18}NS_2})_2(\mathrm{C_{12}H_8N_2})]\cdot0.5\mathrm{C_2H_6O}$, (I), and bis(*N*,*N*-di-*n*-hexyldithiocarbamato-$\kappa^2S,S'$)bis(1,10-phenanthroline-$\kappa^2N,N'$)calcium(II), $[\mathrm{Ca}(\mathrm{C_{13}H_{26}NS_2})_2(\mathrm{C_{12}H_8N_2})_2]$, (II), are mixed-ligand complexes. In the first compound, the Zn atom has a distorted octahedral coordination, while in the second compound, the Ca atom is eight-coordinate, with four S and four N atoms forming a highly distorted cube.

## Comment

During an investigation of the antioxidant properties of metal dithiocarbamate additives (Becker & Knorr, 1996; Becker *et al.*, 1996) in vegetable oils for technical applications, a series of model compounds has been prepared. The crystal structures of zinc dithiocarbamates designed for improved activity (Reck & Becker, 2003*a*) and of oxidized derivatives believed to play a role as intermediates in the antioxidant action of zinc dithiocarbamates (Reck *et al.*, 1995; Reck & Becker, 2003*b*) have already been published. Against this background, we present here the crystal structures of the two title complexes, (I) and (II).



(I) $M$ = Zn, $R$ = *n*-Bu, $x$ = 2, $y$ = 1, ethanol hemisolvate
(II) $M$ = Ca, $R$ = *n*-hexyl, $x$ = 2, $y$ = 2

While calcium dithiocarbamates themselves were observed to be unstable, the 1,10-phenanthroline complex of calcium dihexyldithiocarbamate, (II), is stable and displays a rare eightfold coordination, formed by four N atoms of two phenanthroline ligands and four S atoms of two dihexyldithiocarbamate ligands. These eight atoms form a highly distorted cube. The average Ca—N and Ca—S distances are 2.59 (3) and 2.96 (6) Å, respectively. The bite distances of the phenanthroline and dithiocarbamate ligands are N1$\cdots$N14 = 2.723 (5) Å, N15$\cdots$N28 = 2.721 (5) Å, S29$\cdots$S30 = 2.949 (3) Å and S31$\cdots$S32 = 2.948 (3) Å.

In contrast with (II), zinc dithiocarbamate forms a complex, (I), with only one 1,10-phenanthroline ligand. Two N atoms of the phenanthroline ligand and four S atoms of two dibutyldithiocarbamate molecules form a distorted octahedron. The coordinative bonds in (I) are significantly shorter than the corresponding bonds in (II). The average Zn—N and Zn—S distances are 2.23 (7) and 2.51 (6) Å, respectively. The bite distances of the ligands in (I) are N1$\cdots$N14 = 2.671 (5) Å, S15$\cdots$S16 = 2.929 (3) Å and S17$\cdots$S18 = 2.902 (3) Å.

The phenanthroline ligands in (I) and (II) are almost planar; the corresponding r.m.s. deviations are 0.035, 0.039 and 0.029 Å, respectively. The dihedral angle between the two symmetry-independent phenanthroline molecules in (II) is 78.84 (4)°.

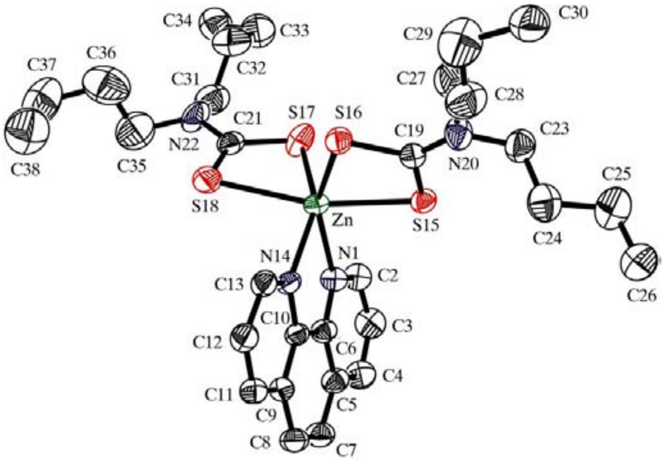


**Figure 1**
The molecular structure of (I), showing 30% probability displacement ellipsoids. The ethanol solvent molecule and all H atoms have been omitted for clarity.

In (I), as well as in (II), there are $\pi$–$\pi$ interactions between symmetry-related phenanthroline ligands. These interactions are defined by the distances between the ring centroids (DC), the perpendicular distance of the centroid of one ring from the plane of the other (DP) and the interplanar angle. For compound (I), the numerical values of these parameters are as follows: for ring C5–C10 and ring C9–C13/N14 at ($1 - x$, $-y$, $2 - z$), DC = 3.632 (2) Å, DP = 3.318 and 3.350 Å, and angle = 2.76°; for ring C9–C13/N14 and ring C9–C13/N14 at ($1 - x$, $-y$, $2 - z$), DC = 3.682 (2) Å, DP = 3.371 Å and angle = 0°. For compound (II), these parameters are as follows: for ring C5–C10 and ring C9–C13/N14 at ($2 - x$, $1 - y$, $-z$), DC = 3.7726 (18) Å, DP = 3.642 and 3.610 Å, and angle = 2.60°; for ring C19–C24 and ring C23–C27/N28 at ($1 - x$, $-y$, $-z$), DC = 3.7436 (18) Å, DP = 3.682 and 3.703 Å, and angle = 2.22°.

DOI: 10.1107/S0108270104001441

The crystal structure of (I) contains half an ethanol molecule per complex molecule. The butyl groups in (I) and the hexyl groups in (II) show large displacement parameters, indicating weak hydrophobic interactions between the complex molecules.

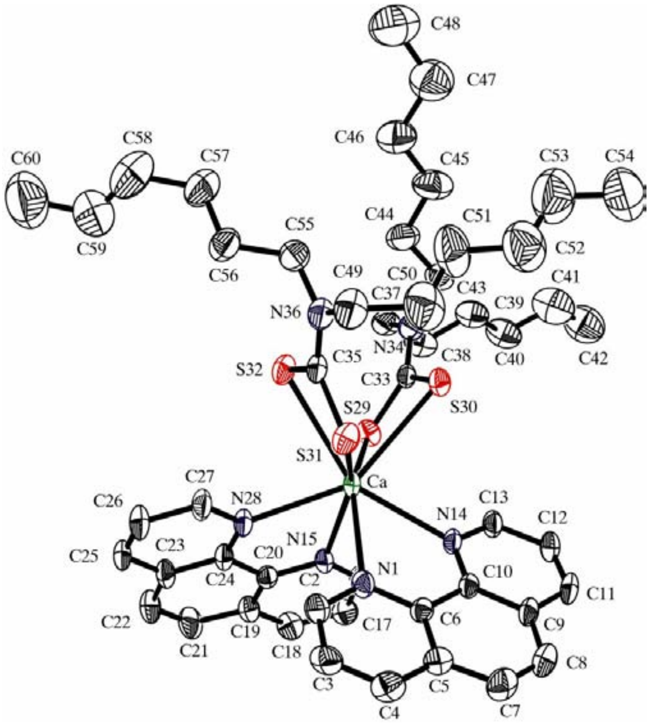


**Figure 2**
The molecular structure of (II), showing 30% probability displacement ellipsoids. All H atoms have been omitted for clarity.

## Experimental

For the preparation of (I), a stirred solution of zinc di-*n*-butyldithiocarbamate in ethanol was treated with a solution of 1,10-phenanthroline (2.2 mole equivalent) in ethanol at ambient temperature. After addition of water, a yellow precipitate was collected and recrystallized from ethanol–water (1:1). Yellow crystals of (I) were obtained (m.p. 461–462 K). Spectroscopic analysis: IR ($\nu$, cm$^{-1}$): 3050, 2970, 2925, 2860, 1625, 1595, 1570, 1515, 1500, 1470, 1465, 1425, 1405, 1370, 1355, 1350, 1305, 1300, 1290, 1255, 1240, 1255, 1210, 1195, 1180, 1140, 1105, 1090, 1045, 990, 955, 865, 850, 775, 740, 730, 720. For the preparation of (II), di-*n*-hexylamine (1.0 mole equivalent) and carbon disulfide (1.2 mole equivalent) were added to a stirred aqueous solution of sodium hydroxide (1.1 mole equivalent). The mixture was kept at 273 K for 30 min and then allowed to reach ambient temperature. An aqueous solution of calcium chloride (0.7 mole equivalent) was then added, followed by the addition of a solution of 1,10-phenanthroline (2.2 mole equivalent). The yellow precipitate obtained was recrystallized from ethanol–water (1:1), giving yellow crystals of (II) (m.p. 441 K). Spectroscopic analysis: IR ($\nu$, cm$^{-1}$): 3010, 2940, 2910, 2850, 1610, 1580, 1575, 1565, 1505, 1465, 1415, 1405, 1360, 1250, 1240, 1205, 1175, 1130, 1100, 1085, 980, 950, 940, 925, 885, 845, 830, 800, 725, 720, 690.

## Compound (I)

*Crystal data*

$[Zn(C_9H_{18}NS_2)_2(C_{12}H_8N_2)]\cdot 0.5C_2H_6O$
$M_r = 677.34$
Triclinic, $P\bar{1}$
$a = 10.006$ (4) Å
$b = 13.347$ (2) Å
$c = 15.531$ (2) Å
$\alpha = 103.710$ (10)°
$\beta = 102.78$ (2)°
$\gamma = 108.37$ (2)°
$V = 1811.2$ (8) Å$^3$
$Z = 2$
$D_x = 1.242$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–20°
$\mu = 0.94$ mm$^{-1}$
$T = 293$ (2) K
Prismatic, yellow
0.32 × 0.29 × 0.28 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
6383 measured reflections
6383 independent reflections
5232 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 0.4%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.149$
$S = 1.21$
6383 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 0.79$ e Å$^{-3}$
$\Delta\rho_{min} = -0.28$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Zn—N14 | 2.178 (2) | Zn—S15 | 2.4793 (11) |
| Zn—N1 | 2.284 (2) | Zn—S16 | 2.5083 (9) |
| Zn—S17 | 2.4605 (10) | Zn—S18 | 2.6012 (14) |
| | | | |
| N14—Zn—N1 | 73.48 (8) | N14—Zn—S18 | 86.24 (6) |
| N1—Zn—S15 | 85.01 (7) | S17—Zn—S18 | 69.90 (4) |
| S17—Zn—S15 | 103.22 (4) | S15—Zn—S18 | 165.37 (3) |
| S15—Zn—S16 | 71.92 (3) | S16—Zn—S18 | 97.29 (4) |

## Compound (II)

*Crystal data*

$[Ca(C_{13}H_{26}NS_2)_2(C_{12}H_8N_2)_2]$
$M_r = 921.42$
Triclinic, $P\bar{1}$
$a = 11.875$ (4) Å
$b = 13.129$ (2) Å
$c = 17.547$ (4) Å
$\alpha = 72.290$ (10)°
$\beta = 80.91$ (2)°
$\gamma = 84.20$ (2)°
$V = 2569.2$ (11) Å$^3$
$Z = 2$
$D_x = 1.191$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–20°
$\mu = 0.32$ mm$^{-1}$
$T = 293$ (2) K
Prismatic, yellow
0.30 × 0.28 × 0.25 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
9086 measured reflections
9086 independent reflections
7339 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.1°$
$h = -13 \rightarrow 14$
$k = -14 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 0.4%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.155$
$S = 1.07$
9086 reflections
550 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1184P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.82$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.24$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Ca—N28 | 2.5571 (15) | Ca—S29 | 2.8981 (11) |
| Ca—N14 | 2.5616 (15) | Ca—S31 | 2.9114 (11) |
| Ca—N15 | 2.6145 (18) | Ca—S32 | 2.9963 (8) |
| Ca—N1 | 2.6333 (19) | Ca—S30 | 3.0371 (8) |
| | | | |
| N28—Ca—N15 | 63.48 (5) | S29—Ca—S32 | 85.16 (3) |
| N28—Ca—N1 | 78.98 (6) | S31—Ca—S32 | 59.85 (3) |
| N14—Ca—N1 | 63.20 (5) | N14—Ca—S30 | 78.73 (4) |
| N15—Ca—S29 | 71.63 (4) | S29—Ca—S30 | 59.54 (2) |
| N1—Ca—S31 | 73.59 (5) | S31—Ca—S30 | 83.69 (3) |
| N28—Ca—S32 | 78.80 (4) | | |

The crystal structure of (I) contains one ethanol molecule per unit cell. The ethanol molecule lies close to the inversion centre at $(0,\frac{1}{2},1)$, resulting in ethanol atom O1*E* being only 1.908 (18) Å from ethanol atom C2*E* at $(-x, 1 - y, 2 - z)$; all ethanol atoms were then given an occupancy factor of 0.5. The H atoms of (I) and (II) were positioned corresponding to their geometrical conditions and refined using a riding model. The hydroxyl H atom of the ethanol molecule in (I) could not be located.

For both compounds, data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL*97.

The authors cordially thank Mrs G. Bannier for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1638). Services for accessing these data are described at the back of the journal.

## References

Becker, R. & Knorr, A. (1996). *Lubr. Sci.* **8**, 95–117.
Becker, R., Knorr, A. & Kelm, J. (1996). *Oxid. Commun.* **19**, 33–43.
Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Reck, G. & Becker, R. (2003*a*). *Acta Cryst.* E**59**, m234–m235.
Reck, G. & Becker, R. (2003*b*). *Acta Cryst.* E**59**, m489–m490.
Reck, G., Becker, R. & Walther, G. (1995). *Z. Kristallogr.* **210**, 769–774.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1999). *SHELXTL-NT*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.