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**Aquabis(3-methyl-4-octanoyl-1-phenyl-5-pyrazolonato-*O,O'*)zinc(II) and Bis(ethanol-*O*)bis(3-methyl-1-phenyl-4-stearoyl-5-pyrazolonato-*O,O'*)cadmium(II)**

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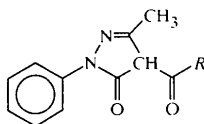
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**Abstract**

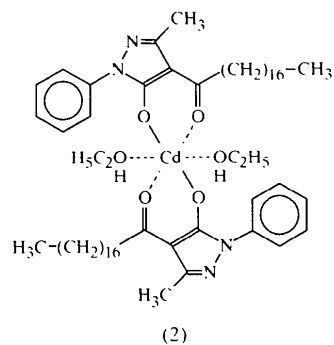
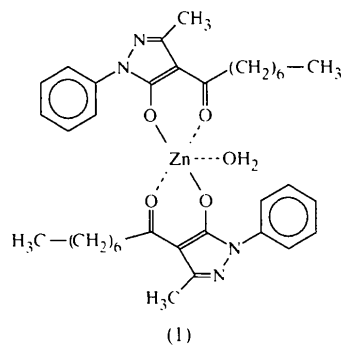
The structures of the zinc and cadmium complexes of 4-acyl-3-methyl-1-phenyl-5-pyrazolones, [Zn(C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)] and [Cd(C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>], show remarkable differences. In the case of zinc, the coordination number is five and a square-pyramidal structure was found, which is realized by the coordination of one molecule of water in the apical position. The coordination polyhedron is significantly distorted towards a trigonal-bipyramidal arrangement. The cadmium compound contains two coordinated ethanol molecules and is octahedral.

**Comment**

4-Acyl-3-methyl-1-phenyl-5-pyrazolones are useful agents for the extraction of metals (Jensen, 1959*a,b*; Zolotov & Kuzmin, 1977).



Long-chain 4-acyl-3-methyl-1-phenyl-5-pyrazolones can be used likewise as carriers in the liquid membrane permeation of copper (Mickler *et al.*, 1991; Kümmel *et al.*, 1996), as well as in the competing permeation of nickel, zinc and cadmium (Mickler *et al.*, 1996). In this case, zinc is selected before cadmium and nickel, even though the stability constants of complexes with 4-acyl-5-pyrazolones show the reverse sequence (Friedrich *et al.*, 1989). In order to clarify any influences of structural parameters on this behaviour, the molecular structures of the zinc and cadmium complexes with long-chain 4-acyl-3-methyl-1-phenyl-5-pyrazolones, *i.e.* (1) and (2), respectively, were determined.



In the zinc complex, (1), the central atom displays square-pyramidal coordination, strongly distorted towards trigonal-bipyramidal coordination (Fig. 1). Characteristic of the distortion are the angles about the Zn atom: 161.1 (2) (O11—Zn—O21), 152.2 (2) (O12—Zn—O22), 104.3 (2) (O12—Zn—O3) and 103.5 (2)° (O22—Zn—O3). The Zn—O bond lengths were found to range from 1.970 (3) to 2.061 (4) Å. The C—O and C—C bond lengths within the chelate rings are nearly equal, indicating delocalized  $\pi$  electrons. Both chelate rings are folded about the O donor atoms, by angles of 20.5 (3) and 17.6 (3)°. The planes formed by the chelate and pyrazolone rings are nearly parallel to each other. The double bonds N12=C14 [1.312 (6) Å] and N22=C24 [1.312 (6) Å] are characteristic of the pyrazolone ring. The planes of the phenyl rings are slightly twisted with respect to the pyrazolone planes [charac-

terized by torsion angles of  $-3.7(8)$  and  $-14.7(8)^\circ$ . The complex shows pseudo-twofold symmetry, with the Zn and O3 atoms positioned on the non-crystallographic twofold axis. Intermolecular hydrogen bonds were found between atoms O3 and N12 *via* H10, as well as between atoms O3 and N22 *via* H20. Thus, each molecule is linked to two others, forming infinite chains. The  $H10 \cdots N12$  bonds are located nearly parallel to *b*, but the  $H20 \cdots N22$  bonds are oriented parallel to the *ab* plane. The molecule itself lies somewhere between being parallel to the [101] plane and parallel to the [111] plane. The structure is closely related to that of aquabis(acetylacetonato)zinc (Lippert & Truter, 1960), which was also described as trigonal bipyramidal, whereas bis(benzoylacetonato)(ethanol)zinc (Belford *et al.*, 1969) was observed to be more square pyramidal. However, any similar zinc chelates including the pyrazolone moiety are not known.

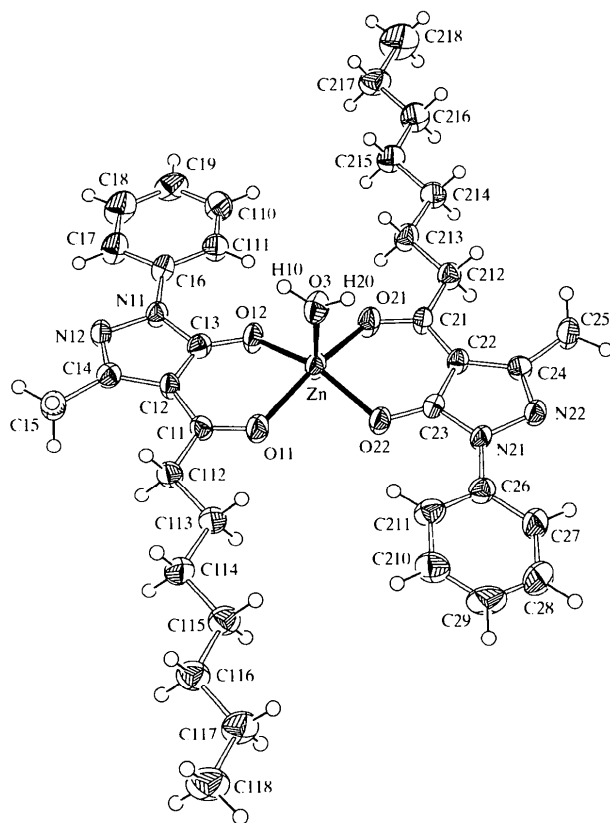


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids and H atoms as spheres of arbitrary radii.

The cadmium complex, (2), has an octahedral coordination polyhedron (Fig. 2). Besides two pyrazolone ligands, the Cd atom binds two molecules of ethanol. An analogous structure was found for bis(ethanol)bis(4-benzoyl-3-methyl-1-phenyl-5-pyrazolonato)calcium

(Uhlemann *et al.*, 1995). The central  $CdO_4$  ring is perfectly planar as a result of the fact that the Cd atom lies on a crystallographic inversion centre. The Cd—O bond lengths are 2.193(3) and 2.268(3) Å. There is a somewhat greater distance [2.332(4) Å] to the oxygen donors of the coordinated solvent molecules. The angles between the best planes are similar to those in the zinc complex. Again, while the chelate and pyrazolone rings are nearly coplanar, the value of the angle describing the fold of the chelate ring about the donor O atoms is  $2.8(2)^\circ$ . The torsion angle between the phenyl and heterocyclic ring planes is  $-7.5(5)^\circ$ . Intermolecular hydrogen bonds were found between atoms O3 and N2, forming chains parallel to the *a* axis. While some cadmium reference compounds with the  $\beta$ -diketone structural element are well known, *e.g.* bis(acetylacetonato)(1,10-phenanthroline)cadmium (Bustos *et al.*, 1983), examples with the pyrazolone fragment have not been reported.

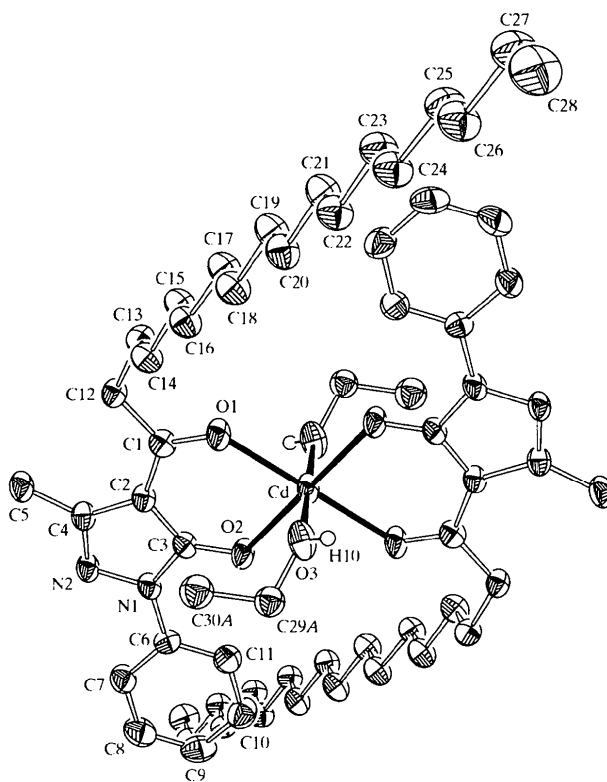


Fig. 2. The molecular structure of (2) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

### Experimental

The title compounds were synthesized by adding ethanolic solutions of  $Zn(CH_3COO)_2 \cdot 2H_2O$  and  $Cd(CH_3COO)_2 \cdot 2H_2O$ , respectively, to stirred warm solutions of 3-methyl-4-octanoyl-1-phenyl-5-pyrazolone and 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone (Mickler & Uhlemann, 1993) in ethanol. The products were recrystallized from ethanol. In the case of

the cadmium complex, only some long needles were suitable for analysis. Attempts to cut them without damage were unsuccessful.

### Compound (1)

#### Crystal data

[Zn(C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]

$M_r = 682.15$

Triclinic

$P\bar{1}$

$a = 10.181 (5) \text{ \AA}$

$b = 13.047 (7) \text{ \AA}$

$c = 14.751 (7) \text{ \AA}$

$\alpha = 101.60 (3)^\circ$

$\beta = 101.90 (4)^\circ$

$\gamma = 99.86 (5)^\circ$

$V = 1831.3 (16) \text{ \AA}^3$

$Z = 2$

$D_x = 1.237 \text{ Mg m}^{-3}$

$D_m$  not measured

#### Data collection

Stoe Stadi-4 diffractometer

$\omega/2\theta$  scans

Absorption correction: none

4209 measured reflections

4209 independent reflections

2732 reflections with

$I > 2\sigma(I)$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 42

reflections

$\theta = 12.5\text{--}15.0^\circ$

$\mu = 0.715 \text{ mm}^{-1}$

$T = 210 (2) \text{ K}$

Needle

$0.42 \times 0.08 \times 0.08 \text{ mm}$

Colourless

$\theta_{\max} = 21.7^\circ$

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = 0 \rightarrow 15$

2 standard reflections

frequency: 120 min

intensity decay: none

#### Refinement

Refinement on  $F^2$

$R(F) = 0.051$

$wR(F^2) = 0.117$

$S = 1.054$

4209 reflections

421 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.320 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.427 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

### Compound (2)

#### Crystal data

[Cd(C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>]

$M_r = 1083.82$

Triclinic

$P\bar{1}$

$a = 8.817 (6) \text{ \AA}$

$b = 9.361 (7) \text{ \AA}$

$c = 19.06 (2) \text{ \AA}$

$\alpha = 101.48 (7)^\circ$

$\beta = 99.58 (9)^\circ$

$\gamma = 99.10 (9)^\circ$

$V = 1490 (2) \text{ \AA}^3$

$Z = 1$

$D_x = 1.208 \text{ Mg m}^{-3}$

$D_m$  not measured

#### Data collection

Stoe Stadi-4 diffractometer

$\omega/2\theta$  scans

Absorption correction: none

7182 measured reflections

3581 independent reflections

3262 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.081$

#### Refinement

Refinement on  $F^2$

$R(F) = 0.042$

$wR(F^2) = 0.096$

$S = 0.983$

3577 reflections

328 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2$

$+ 0.5226P]$

where  $P = (F_o^2 + 2F_c^2)/3$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 56

reflections

$\theta = 12.5\text{--}15.0^\circ$

$\mu = 0.416 \text{ mm}^{-1}$

$T = 210 (2) \text{ K}$

Needle

$1.61 \times 0.15 \times 0.15 \text{ mm}$

Colourless

$\theta_{\max} = 25^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -15 \rightarrow 15$

2 standard reflections

frequency: 120 min

intensity decay: none

$(\Delta/\sigma)_{\max} = 0.009$

$\Delta\rho_{\max} = 0.490 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.014 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1)

Zn—O22	1.970 (3)	N11—C16	1.430 (6)
Zn—O12	1.979 (4)	N12—C14	1.312 (6)
Zn—O3	2.001 (4)	N21—C23	1.366 (6)
Zn—O21	2.029 (4)	N21—N22	1.407 (6)
Zn—O11	2.061 (4)	N21—C26	1.418 (7)
N11—C13	1.373 (6)	N22—C24	1.312 (6)
N11—N12	1.400 (6)		
O22—Zn—O12	152.2 (2)	C13—N11—N12	110.8 (4)
O22—Zn—O3	103.5 (2)	C14—N12—N11	106.3 (4)
O12—Zn—O3	104.3 (2)	C11—O11—Zn	129.8 (3)
O22—Zn—O21	89.68 (15)	C13—O12—Zn	121.4 (3)
O12—Zn—O21	85.7 (2)	O11—C11—C12	121.1 (5)
O3—Zn—O21	98.6 (2)	C14—C12—C13	105.9 (4)
O22—Zn—O11	87.86 (15)	C13—C12—C11	121.7 (5)
O12—Zn—O11	87.7 (2)	O12—C13—C12	132.0 (5)
O3—Zn—O11	100.3 (2)	N11—C13—C12	105.7 (4)
O21—Zn—O11	161.1 (2)	N12—C14—C12	111.3 (5)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (1)

D—H...A	D—H	H...A	D...A	D—H...A
O3—H10...N12 <sup>i</sup>	0.92 (4)	1.87 (4)	2.760 (6)	162 (5)
O3—H20...N22 <sup>ii</sup>	0.92 (4)	1.85 (4)	2.742 (6)	162 (5)

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $-x, -y, 1 - z$ .

Table 3. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

Cd—O2	2.193 (3)	N2—C4	1.319 (4)
Cd—O1	2.268 (3)	O1—C1	1.246 (4)
Cd—O3	2.332 (4)	O2—C3	1.274 (4)
N1—C3	1.382 (4)	C1—C2	1.445 (5)
N1—N2	1.390 (4)	C2—C3	1.414 (5)
N1—C6	1.423 (4)	C2—C4	1.438 (5)
O2'—Cd—O1'	82.70 (10)	C1—O1—Cd	133.2 (2)
O2—Cd—O1'	97.30 (10)	C3—O2—Cd	125.0 (2)
O2'—Cd—O3	87.35 (12)	O1—C1—C2	121.4 (3)
O2—Cd—O3	92.65 (12)	C3—C2—C4	104.9 (3)
O1'—Cd—O3	89.15 (13)	C3—C2—C1	124.6 (3)
O1—Cd—O3	90.85 (13)	O2—C3—C2	132.9 (3)
C3—N1—N2	110.9 (3)	N1—C3—C2	106.3 (3)
C4—N2—N1	106.7 (3)	N2—C4—C2	111.2 (3)

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

Table 4. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (2)

D—H...A	D—H	H...A	D...A	D—H...A
O3—H10...N2 <sup>i</sup>	0.73 (5)	2.07 (5)	2.789 (5)	173 (5)

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

The crystals of the zinc compound were of poor quality and so reflections could only be monitored up to  $\theta = 21.7^\circ$ . The structures were solved by direct methods and successive difference Fourier syntheses. All of the phenyl and alkyl H atoms were calculated and refined as riding atoms. The hydroxy H atom (H10) of the cadmium complex was located from the difference map and refined freely. In the zinc compound, only the positions, not the  $U$ 's, of the water H atoms were refined, to produce better bond lengths. All non-H atoms were refined with anisotropic displacement parameters, with the exception of the disordered atoms C29A/B and C30A/B of the solvent molecule in the cadmium complex. These atoms were refined isotropically using split positions (0.5 occupancy factor for each). Bond-length restraints were employed for the C29A/B—C30A/B bonds, as well as for the O3—C29A/B bonds. The greatest hole ( $-1.01 \text{ e } \text{Å}^{-3}$ ) in the difference electron-density map was found to be near the Cd atom (distance 1.13 Å).

For both compounds, data collection: *STADIA* (Stoe & Cie, 1995a); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1995b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1970).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1020). Services for accessing these data are described at the back of the journal.

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