

Two one-dimensional zinc(II) coordination polymers: *catena*-poly[[bis-(pentane-2,4-dionato- κ^2 O,O')zinc]- μ -1,4-bis(*x*-pyridyl)-2,3-diazabuta-1,3-diene] (*x* = 3, 4)

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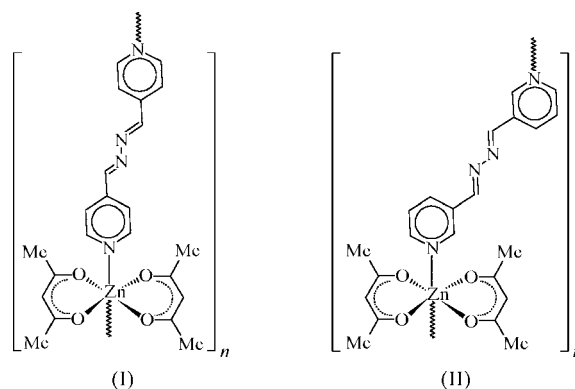
The structures of the two title isomeric compounds, $[\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]_n$, are built up around two non-equivalent symmetry centres, one of them at the cation position and the other bisecting the N—N bond in the 1,4-bis(3/4-pyridyl)-2,3-diazabuta-1,3-diene (3pdb/4pdb) units. Both Zn cations have the Zn atoms an inversion centres and present tetragonally distorted octahedral environments, but differences in their linkage through the 3pdb and 4pdb ligands give rise to differently shaped weakly interacting chains.

Comment

The exobidentate bis-pyridyl ligand 1,4-bis(4-pyridyl)-2,3-diazabuta-1,3-diene (4pdb) has been reported to form coordination polymers with several metal centres (Co^{II} , Cd^{II} , Ni^{II} , Ag^{I} , Mn^{II} and Pb^{II}) containing diverse counter-ions (NO_3^- , SCN^- , I^- and saccharinate) (Ciurtin *et al.*, 2001; Kallil *et al.*, 2005; Shen, 2003; Shi, Li, Li *et al.*, 2002; Shi, Li, Tong *et al.*, 2002). These polymeric complexes usually present interesting structural topologies, but recently it has been reported that the reaction of zinc perchlorate hexahydrate with the bis-pyridyl ligand 4pdb, under mild conditions, results in the formation of a non-polymeric compound, *viz.* $[\text{Zn}(\text{4pdb})_2(\text{MeOH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{pdb} \cdot 1.72\text{MeOH} \cdot 1.28\text{H}_2\text{O}$ (Shoshnik *et al.*, 2005), hereafter (III), with a [2+2+2]-octahedral coordination environment around the zinc ion and a *trans* configuration of the related coordinated species 4pdb, MeOH and H_2O . Thus, the pyridyl N atoms of two molecules of 4pdb are bonded axially to the solvated cationic fragment $[\text{Zn}(\text{MeOH})_2(\text{H}_2\text{O})_2]^{2+}$, giving rise to a linear N—Zn^{II}—N oligomer. The pyridyl rings of adjacent oligomers are

ordered in a such a way as to promote π – π stacking interactions.

In the present work, we report on the structural differences found when the neutral ligands providing the O-donor atoms to the $[\text{Zn}(\text{MeOH})_2(\text{H}_2\text{O})_2]^{2+}$ oligomer core in (III) (*viz.* water and methanol) are replaced by a different O-donor ligand, the β -diketonate acetylacetonate (acac), through the $\text{Zn}(\text{acac})_2$ complex. In contrast to the above $[\text{Zn}(\text{MeOH})_2(\text{H}_2\text{O})_2]^{2+}$ dication, the reaction product of $\text{Zn}(\text{acac})_2$ with the divergent 4pdb ligand is a polymeric species, $[\text{Zn}(\text{acac})_2(\text{4pdb})]_n$, (I). As a comparison with the 4pdb case, the 3-pyridyl isomer 1,4-bis(3-pyridyl)-2,3-diazabuta-1,3-diene (3pdb) was also included in this study. The resulting coordination polymer, $[\text{Zn}(\text{acac})_2(\text{3pdb})]_n$, (II), shows that the 3pdb ligand likewise acts as a spacer, with the $\text{Zn}(\text{acac})_2$ complex as a node.



Figs. 1 and 2 show ellipsoid plots for (I) and (II), respectively; Tables 1 and 2, in turn, give selected coordination bond lengths and angles. The structures are built up around two non-equivalent symmetry centres, one at the cation position and the other bisecting the N—N bond in the 3pdb or 4pdb unit. Both compounds present tetragonally distorted octahedral environments around Zn, with the O atoms of two chelating acac groups in the equatorial positions and the pyridyl N atoms as apices. Structure (I) shows a slightly larger departure from ideal C_{4v} geometry, both in the Zn—O lengths and in the O—Zn—N angles (see Table 1), with a slightly larger apical deviation from the normal to the mean equatorial plane [$178.5(1)$ versus $179.9(1)^\circ$]. While the Zn—N bond distances in the two compounds [$2.2689(17)$ Å in (I) and $2.271(3)$ Å in (II)] are very similar, they are significantly longer than the corresponding bond in the related Zn^{II} complex, (III), where the Zn—N bond length is $2.120(2)$ Å. This enlargement could be attributed to a less attractive effect towards the metal centre, due to an increase of its negative charge when the neutral ligands (water and methanol) are replaced by the anionic acac. On the other hand, a shortening of the Zn—O distances should be expected in the polymeric complexes considering the charge effect of the acac anion, which implies a stronger interaction of the acetylacetonate O atoms than those of the water and methanol molecules. In fact, this is actually observed; the Zn—O lengths for (I) and (II) lie in the range $2.0328(13)$ – $2.0617(13)$ Å compared with a range of $2.0977(18)$ – $2.1642(19)$ Å in (III). In both cases, the

structures organize as chains [running along $[21\bar{1}]$ and $[201]$ for (I) and (II), respectively], where the bridging links are the 4pdb and 3pdb ligands. These are, in turn, responsible for the different geometries observed in the one-dimensional structures, through the diverse disposition of their N atoms and the associated differences in binding modes. In fact, while in (II) the lateral N3 bite of the 3pdb ligand generates zigzag chains, the more linear 4pdb ligand gives rise to very straight one-dimensional chains in (I). This difference can be assessed quantitatively by considering the angle between the apical axis

in each coordination polyhedron and the direction of maximum span of the corresponding 4pdb or 3pdb connecting ligands, *viz.* almost linear in (I) [$172.1(1)^\circ$] and quite broken in (II) [$128.2(1)^\circ$] (see Figs. 3 and 4).

The two structures are similar in favouring the aggregation of chains related by a $[100]$ shift, suggesting some kind of two-dimensional structure parallel to (011) in the case of (I) and to (010) in (II). However, only in the second case does there seem to be a clear $C-H \cdots O$ hydrogen-bonding interaction [$C7-H7 \cdots O15(1+x, y, z)$, with $H \cdots O = 2.41 \text{ \AA}$,

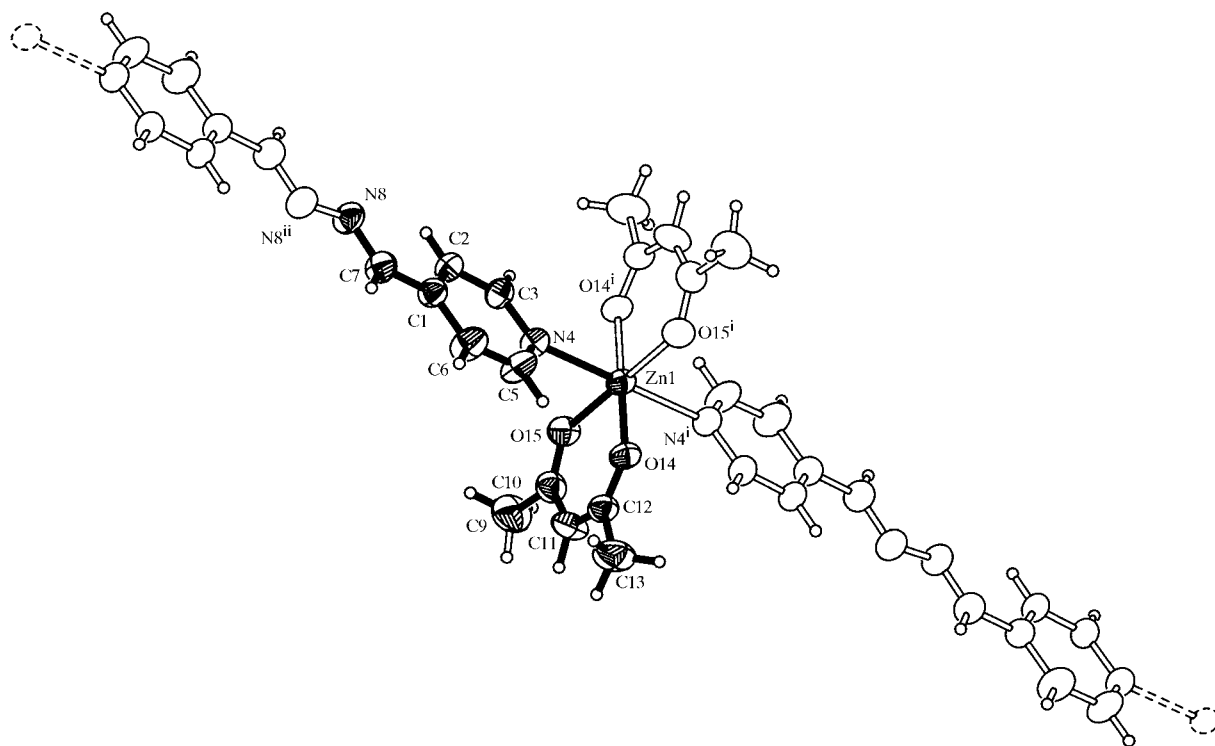


Figure 1

A molecular diagram of (I), showing the way in which the chains are formed. Atom numbering is shown only in the independent part of the coordination polyhedron, which is drawn with full displacement ellipsoids (40% probability level). [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x - 1, y, -z + 2$.]

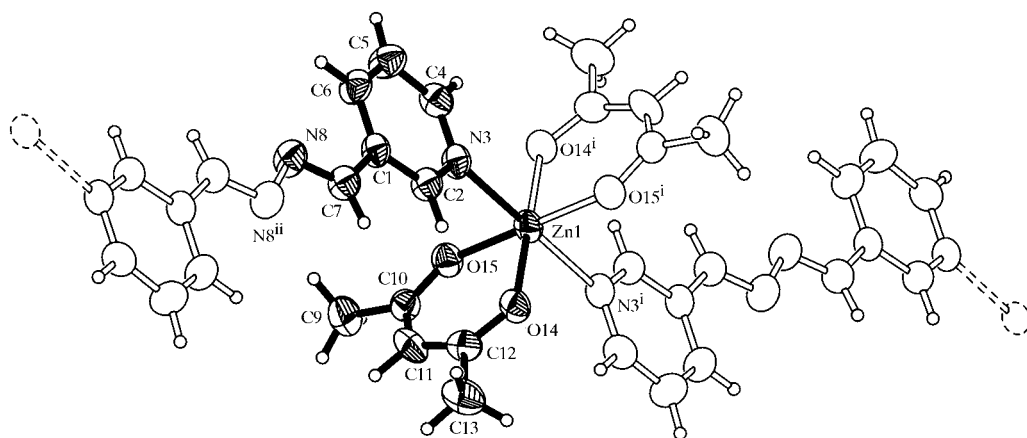


Figure 2

A molecular diagram of (II), showing the way in which the chains are formed. Atom numbering is shown only in the independent part of the coordination polyhedron, which is drawn with full displacement ellipsoids (40% probability level). [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x - 1, y, -z + 2$.]

$C \cdots O = 3.333(4) \text{ \AA}$ and a very favourable $C-H \cdots O$ angle of 176° (Desiraju, 1996); see Fig. 4]. In (I), instead, only feeble $C-H \cdots O$ contacts link neighbouring chains, with a lower boundary for the $H \cdots O$ distances of 2.65 \AA and $C-H \cdots O$ angles not larger than 130° . The different chain geometries can, in principle, provide plausible arguments for explaining this behaviour; while in both compounds the 3pdb or 4pdb ligands form a near planar structure, with the pyridyl rings perpendicular to the $O15-Zn1-O15^i$ axis [symmetry code: (i) $-x + 1, -y + 1, -z + 1$], only in (II) does this disposition allow the acidic non-aromatic $C7-H7$ donor group in the zigzag chain to be close to acetylacetonate atom $O15$. In the

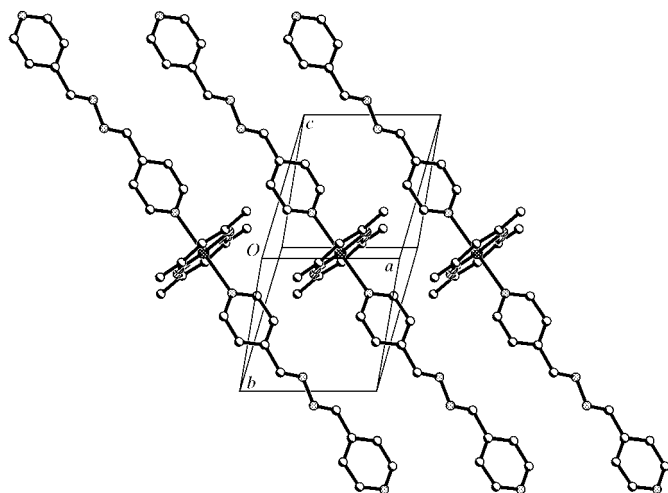


Figure 3
The packing of (I), viewed down [011], showing the organization of chains into planes parallel to (010) through a [100] shift. H atoms have been omitted.

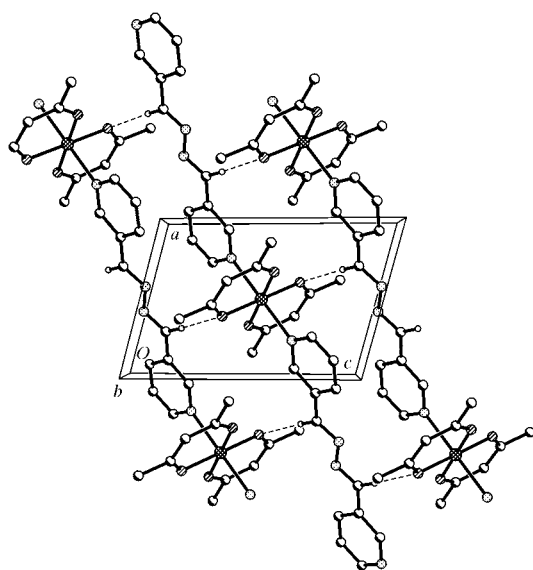


Figure 4
The packing of (II), viewed down the [010] axis, showing the organization of chains into planes parallel to (010) through a [100] shift. Interchain $C-H \cdots O$ bonds are drawn with broken lines. H atoms not involved in hydrogen bonding have been omitted.

most linear structure, (I), a distinct situation occurs; the aromatic groups $C2-H2$ and $C3-H3$ are closer to atom $O15$, thereby shielding it from an eventual interaction with the $C7-H7$ moiety. Consequently, the particular chain disposition in (II) would more likely correlate with a denser packing than (I), which is confirmed when the calculated densities for the two isomers are compared [1.390 Mg m^{-3} for (I) and 1.437 Mg m^{-3} for (II)].

Experimental

All solvents were purchased from commercial sources and used without further purification. $Zn(acac)_2$ was obtained from Merck. The 3pdb (Dong *et al.*, 2000) and 4pdb (Ciurtin *et al.*, 2001) ligands were prepared following literature procedures. The coordination polymers $[Zn(acac)_2(3pdb)]_n$ and $[Zn(acac)_2(4pdb)]_n$ were prepared in a similar manner from the reaction of an excess of $Zn(acac)_2$ with the appropriate bidentate Schiff base. The procedure, exemplified in what follows for the 3pdb compound, consisted in dissolving the ligand (8.3 mg, 0.040 mmol) in MeOH (3.0 ml). A methanol solution (3.0 ml) of $Zn(acac)_2$ (20.8 mg, 0.080 mmol) was then added and the mixture was stirred for 1 min. After 30 h in a closed container, yellow crystals suitable for X-ray diffraction were filtered off, washed firstly with MeOH ($3 \times 3.0 \text{ ml}$) and then with diethyl ether ($3 \times 3.0 \text{ ml}$), and finally dried in air.

Isomer (I)

Crystal data

$[Zn(C_5H_7O_2)_2(C_{12}H_{10}N_4)]$
 $M_r = 473.82$
 Triclinic, $P\bar{1}$
 $a = 6.3525(8) \text{ \AA}$
 $b = 9.0459(11) \text{ \AA}$
 $c = 10.3907(12) \text{ \AA}$
 $\alpha = 84.282(2)^\circ$
 $\beta = 72.332(2)^\circ$
 $\gamma = 89.558(2)^\circ$
 $V = 565.94(12) \text{ \AA}^3$

$Z = 1$
 $D_x = 1.390 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1870 reflections
 $\theta = 3.3\text{--}26.0^\circ$
 $\mu = 1.12 \text{ mm}^{-1}$
 $T = 273(2) \text{ K}$
 Block, yellow
 $0.20 \times 0.20 \times 0.16 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.81, T_{\max} = 0.84$
 4727 measured reflections

2409 independent reflections
 2293 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 28.0^\circ$
 $h = -7 \rightarrow 7$
 $k = -11 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.097$
 $S = 1.08$
 2409 reflections
 144 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$

Table 1

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

Zn1—O14	2.0328 (13)	Zn1—N4	2.2689 (17)
Zn1—O15	2.0617 (13)		
O14—Zn1—O15	89.51 (5)	O15—Zn1—N4	91.29 (6)
O14—Zn1—N4	89.22 (6)		

Isomer (II)

Crystal data

[Zn(C₅H₇O₂)₂(C₁₂H₁₀N₄)]
M_r = 473.82
 Triclinic, *P* $\bar{1}$
a = 6.8637 (11) Å
b = 8.6257 (14) Å
c = 9.9497 (16) Å
 α = 80.536 (3)°
 β = 73.444 (3)°
 γ = 77.310 (3)°
V = 547.57 (15) Å³

Z = 1
D_x = 1.437 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1134 reflections
 θ = 3.5–25.7°
 μ = 1.16 mm⁻¹
T = 298 (2) K
 Block, yellow
 0.28 × 0.18 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.74, *T_{max}* = 0.88
 4661 measured reflections

2379 independent reflections
 1898 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 28.1°
h = -9 → 8
k = -10 → 10
l = -12 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.054
wR (*F*²) = 0.125
S = 1.04
 2379 reflections
 144 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{Å}^{-3}$

Table 2

Selected geometric parameters (Å, °) for (II).

Zn1—O14	2.037 (2)	Zn1—N3	2.271 (3)
Zn1—O15	2.049 (2)		
O14—Zn1—O15	89.49 (9)	O15—Zn1—N3	89.88 (9)
O14—Zn1—N3	90.04 (9)		

H atoms attached to C atoms were included at their expected positions and allowed to ride [C—H = 0.93 Å and methyl C—H = 0.96 Å, and *U*_{iso}(H) = 1.2*U*_{eq}(C) and 1.5*U*_{eq}(methyl C)]. Methyl groups were allowed to rotate around their local threefold axis.

For both compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3002). Services for accessing these data are described at the back of the journal.

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