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Adducts of bis(acetylacetonato)-zinc(II) with 1,10-phenanthroline and 2,2′-bipyridine

Sanjaya Brahma,[a] H. P. Sachin,[a] S. A. Shivashankar,[a] T. Narasimhamurthy[a] and R. S. Rathore[b]*

[a]Materials Research Center, Indian Institute of Science, Bangalore 560 012, India, and [b]School of Biotechnology, Devi Ahilya University, Indore 452 001, India
Correspondence e-mail: ravindranath_rathore@yahoo.com

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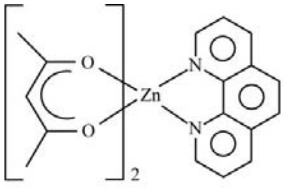
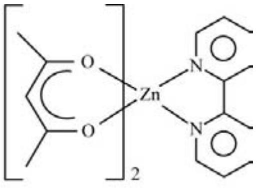
In each of the zinc(II) complexes bis(acetylacetonato-κ^2O,O')(1,10-phenanthroline-κ^2N,N')zinc(II), $[Zn(C_5H_7O_2)_2(C_{12}H_8N_2)]$, (I), and bis(acetylacetonato-κ^2O,O')(2,2′-bipyridine-κ^2N,N')zinc(II), $[Zn(C_5H_7O_2)_2(C_{10}H_8N_2)]$, (II), the metal center has a distorted octahedral coordination geometry. Compound (I) has crystallographically imposed twofold symmetry, with $Z' = 0.5$. The presence of a rigid phenanthroline group precludes intramolecular hydrogen bonding, whereas the rather flexible bipyridyl ligand is twisted to form an intramolecular C—H···O interaction [the chelated bipyridyl ligand is nonplanar, with the pyridyl rings inclined at an angle of 13.4 (1)°]. The two metal complexes are linked by dissimilar C—H···O interactions into one-dimensional chains. The present study demonstrates the distinct effects of two commonly used ligands, *viz*. 1,10-phenanthroline and 2,2′-bipyridine, on the structures of metal complexes and their assembly.

Comment

The ligands 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) are widely used in the design of metallorganic complexes, primarily because of their ability to form stable chelates and to coordinate with various metals (Lever, 2003). From the structural viewpoint, these heterocycles differ in their chelating ability mainly as a result of the difference in the geometry and conformation of the free molecules (Reyzer & Brodbelt, 1999; Oresmaa *et al.*, 2002). Therefore, it is interesting to compare the effects of phen and bipy on metal coordination and more importantly on supramolecular assembly. Towards this aim, Zn^{II}–acetylacetonate (acac) complexes with phen or bipy have been prepared, namely bis(acetylacetonato-κ^2O,O')(1,10-phenanthroline-κ^2N,N')-zinc(II), (I), and bis(acetylacetonato-κ^2O,O')(2,2′-bipyridine-κ^2N,N')zinc(II), (II). These compounds are metal–organic chemical vapor deposition precursors for thin film growth (Williams, 1989; Neelgund *et al.*, 2007, and references therein). The structures and packing of (I) and (II) are compared.



(I)



(II)

The molecules of both (I) and (II), with all adducts in a *cis* geometry, possess C_2 point-group symmetry. However, only in (I), which contains the rigid phen group, is it retained in the crystal ($Z' = 0.5$), with the Zn atom located on the twofold axis; the asymmetric unit comprises one acac ligand and half of the phen ligand (Fig. 1). The bipyridyl system in (II) is substantially distorted, resulting in nonretention of molecular symmetry. Recent database analysis has led to the conclusion that the C_2 point group symmetry is conserved in about 60% of the reported cases (Pidcock *et al.*, 2003).

The Zn—O bonds in (I) and (II) (Figs. 1 and 2) *trans* to the N atoms [2.0441 (12) Å in (I), and 2.0422 (12) and 2.0513 (13) Å in (II)] are shorter than those *trans* to O atoms [2.0853 (13) Å in (I), and 2.0675 (13) and 2.0891 (14) Å in (II)]. A similar but opposite *trans* effect is observed in six-coordinate cobalt complexes (Pasko *et al.*, 2004). The Zn^{II} ions have a distorted octahedral coordination environment, ligated to two acac ligands through the O atoms and to a phen [in (I)] or bipy ligand [in (II)] through the N atoms. The bite distances and angles for (I) and (II), respectively, are as follows: O···O = 2.862 (2) and 2.875 (2)/2.888 (2) Å; N···N = 2.707 (2) and 2.658 (2) Å; O—Zn—O = 87.74 (5) and 88.78 (6)/88.44 (6)°; N—Zn—N = 76.10 (7) and 74.21 (6)°. The differences in

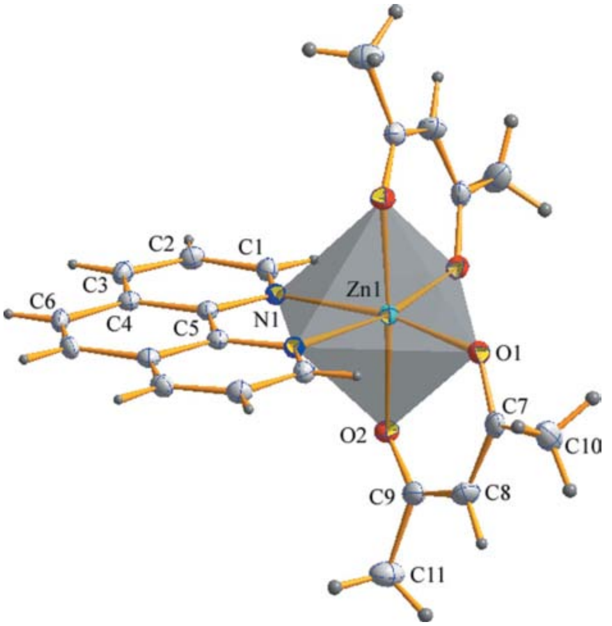


Figure 1
The coordination complex of Zn^{II} with 1,10-phenanthroline, (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

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O···O and N···N bite distances, as well as O—Zn—O and N—Zn—N bite angles, give rise to the distortion from the regular octahedral geometry; compound (II), containing bipy, is slightly more distorted. The distorted octahedral geometry observed here closely resembles that observed in the analogous [*M*(acac)$_2$(phen)] complexes with Mn^{II}, Ni^{II} and V^{III} (Stephens, 1977; Steblyanko *et al.*, 1992; Kavitha, Panchanatheswaran, Elsegood & Dale, 2006), and likewise in the [*M*(acac)$_2$(bipy)] complexes of Co^{II} and V^{III} (Steblyanko *et al.*, 1988; Kameniček *et al.*, 1996; Kavitha, Panchanatheswaran, Low & Glidewell, 2006). The octahedral arrangement is the predominant configuration among six-coordinate transition metal complexes formed by bidentate mixed ligands. A low-energy trigonal–prismatic configuration, as seen in [Mn(acac)$_2$(bipy)] (van Gorkum *et al.*, 2005), is rare. Compound (I) is isomorphous with the Mn^{II} and Ni^{II} complexes (Stephens, 1977; Steblyanko *et al.*, 1992).

The six-membered chelate ring formed by the Zn^{II} and O atoms in (II) is planar. In (I), the ring is slightly puckered and the dihedral angle between the Zn1/O1/O2 and O1/O2/C7–C9 planes, describing the amount of puckering, is 16.8 (1)°. The five-membered chelate ring of Zn^{II} and bipyridyl N atoms is considerably nonplanar, giving rise to an overall nonplanar structure. The flanking pyridyl rings are inclined at a dihedral angle of 13.4 (1)°; the N1—C5—C6—N2 torsion angle is 12.6 (2)°. The dihedral angle in (I) between the acac (O1/O2/C7–C11) and phen (N1/C1–C6) planes is 78.2 (1)°. In (II), the angle between the O1/O2/C11–C15 and O3/O4/C16–C20 acac planes is 73.7 (1)°, and those between the acac planes and the two pyridyl rings range from 68.6 (1) to 85.0 (1)°.

The interactions in (I) and (II) are listed in Tables 1 and 2. The prominent effects of phen and bipy on metal complexes are observed in their assembly. There are no intramolecular interactions in (I), presumably because of the rigidity of the phen group, and partly as a result of the crystallographically imposed symmetry, preventing the donor and acceptor groups coming closer and forming nonbonded interactions. In (II), the bipyridyl system is twisted to accommodate a C10—H10···O3 intramolecular hydrogen bond. The salient feature of the packing in (I) is the intermolecular linkage into a linear chain along the *c* axis *via* C1—H1···O2^{i} hydrogen bonds, as shown in Fig. 3 [symmetry code: (i) $-x, -y+1, -z+1$]. In (II), C4—H4···O1^{ii} interactions [symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z$] are formed by bipy CH atoms, linking molecules into one-dimensional zigzag chains along the *a*-axis direction (Fig. 4). In addition, a short contact, associated with a methyl group [C14—H14*C*···O4^{iii}: H···O = 2.40 Å, C···O = 3.360 (3) Å

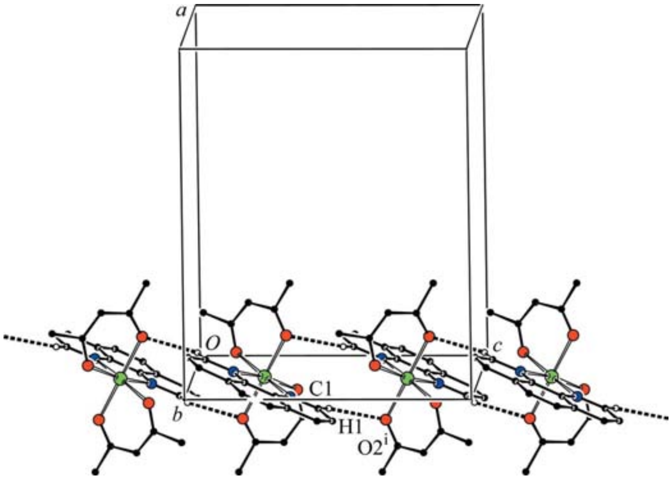

Figure 3
Intermolecular association of metal complexes *via* C—H···O hydrogen bonds into a one-dimensional chain along the [001] direction in (I). Only relevant H atoms are shown. Dashed lines represent hydrogen bonds. [Symmetry code: (i) $-x, -y+1, -z+1$.]

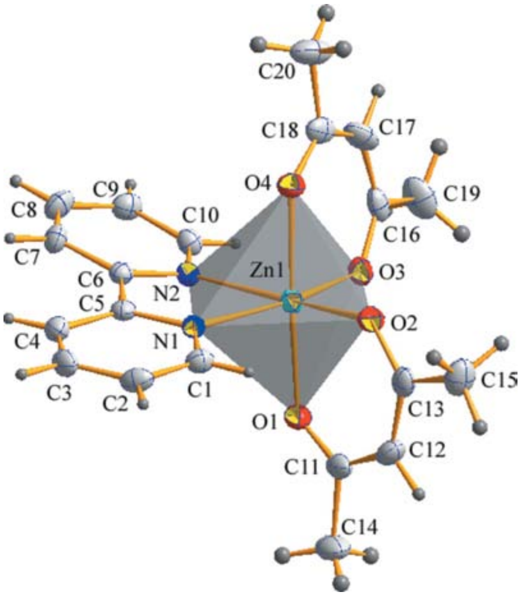

Figure 2
The coordination complex of Zn^{II} with 2,2′-bipyridine, (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

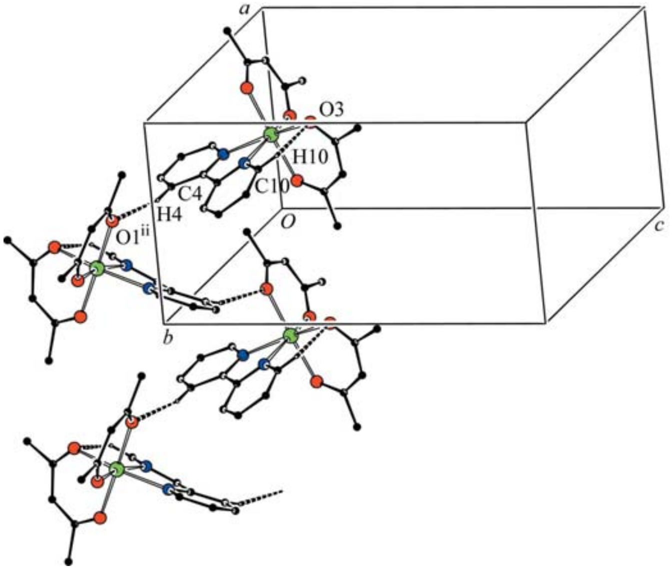

Figure 4
The intermolecular C—H···O hydrogen-bonded one-dimensional zigzag chain of metal complexes along the [100] direction in (II). Dashed lines represent inter- and intramolecular hydrogen bonds. [Symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z$.]

and C—H···O = 176°; symmetry code: (iii) $x + 1$, y, z], is present in (II).

Experimental

Compounds (I) and (II) were synthesized from their precursor hydrate complex, *i.e.* bis(acetylacetonato)aquazinc(II) (Lippert & Truter, 1960; Montgomery & Lingafelter, 1963). Acetylacetone (10 mmol, 1.02 ml) was added to zinc diacetate dihydrate solution (5 mmol, 1.099 g; 30% ethanol–water mixture). Potassium hydroxide (KOH) solution (10 mmol, 0.56 g; 30% ethanol–water mixture) was added gradually to achieve a pH of 6–7. After stirring at room temperature for 1 h, the mixture yielded a precipitate, which was filtered off and dried in a vacuum. The product was recrystallized from ethanol, giving a pure hydrate complex. To obtain (I) and (II) from the respective hydrates, an ethanol solution of the hydrate was prepared and added in a 1:1 molar ratio to ethanol solutions of 1,10-phenanthroline [for (I)] and 2,2′-bipyridine [for (II)]. After stirring at room temperature for 10 min in the case of (I) and 12 h for (II), the adducted compounds precipitated out. The precipitates thus formed were filtered off, washed repeatedly with water and dried in a vacuum [yield = 30 and 82%, and m.p. = 523 and 503 K for (I) and (II), respectively]. Single crystals of (I) and (II) suitable for X-ray diffraction were grown by slow evaporation of methanol solutions.

Compound (I)

Crystal data

$[Zn(C_5H_7O_2)_2(C_{12}H_8N_2)]$
$M_r = 443.79$
Orthorhombic, *Pbcn*
$a = 15.5576\ (11)$ Å
$b = 10.1598\ (7)$ Å
$c = 12.5487\ (9)$ Å
$V = 1983.5\ (2)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.27$ mm^{-1}
$T = 110\ (2)$ K
$0.29 \times 0.25 \times 0.19$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.709$, $T_{\max} = 0.793$
14212 measured reflections
1953 independent reflections
1730 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.080$
$S = 1.09$
1953 reflections
134 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Compound (II)

Crystal data

$[Zn(C_5H_7O_2)_2(C_{10}H_8N_2)]$
$M_r = 419.77$
Orthorhombic, $P2_12_12_1$
$a = 8.1594\ (3)$ Å
$b = 15.3466\ (6)$ Å
$c = 15.5582\ (6)$ Å
$V = 1948.18\ (13)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.29$ mm^{-1}
$T = 110\ (2)$ K
$0.25 \times 0.23 \times 0.18$ mm

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2$^{\rm i}$	0.93	2.58	3.259 (2)	130

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O3	0.93	2.58	3.125 (2)	118
C4—H4···O1$^{\rm ii}$	0.93	2.58	3.484 (3)	164

Symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z$.

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.737$, $T_{\max} = 0.799$
15162 measured reflections
3822 independent reflections
3690 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.052$
$S = 1.10$
3822 reflections
248 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Absolute structure: Flack (1983), 1632 Friedel pairs
Flack parameter: 0.027 (8)

All H atoms were refined using a riding model and fixed individual displacement parameters [$U_{\rm iso}$(H) = $1.2U_{\rm eq}$(aromatic C) or $1.5U_{\rm eq}$(methyl C)]. The methyl groups were allowed to rotate but not to tip. C—H distances were set at 0.93 Å for aromatic and 0.96 Å for methyl H atoms.

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3140). Services for accessing these data are described at the back of the journal.

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