

***mer*-Bis{2,6-bis[1-(4-*tert*-butylphenylimino)ethyl]-pyridine}zinc(II) bis[tris(hexafluoroacetylacetonato)-zincate(II)] diethyl ether hemisolvate**

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Key indicators

Single-crystal X-ray study

$T = 150\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.064\text{ \AA}$

R factor = 0.061

wR factor = 0.129

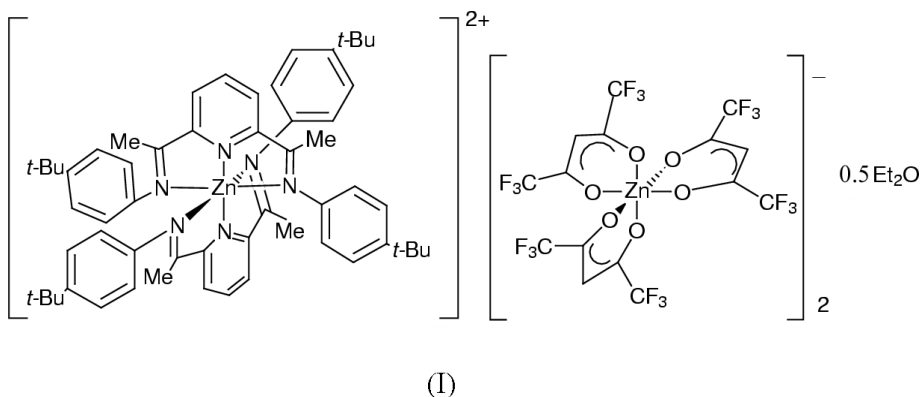
Data-to-parameter ratio = 10.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Reaction of $[\text{Zn}(\text{hfac})_2] \cdot 2\text{H}_2\text{O}$ with L^1 , where hfac and L^1 are hexafluoroacetylacetonate and 2,6-bis[1-(4-*tert*-butylphenylimino)ethyl]pyridine, respectively, results in the formation of $[\text{Zn}(L^1)_2][\text{Zn}(\text{hfac})_3]_2$, *i.e.* $[\text{Zn}(\text{C}_{29}\text{H}_{35}\text{N}_3)_2][\text{Zn}(\text{C}_5\text{HF}_6\text{O}_2)_3]_2 \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$. In the cation, the two L^1 ligands act as *mer*-terdentate ligands. Reaction of $[\text{Zn}(\text{hfac})_2] \cdot 2\text{H}_2\text{O}$ with 2,2':6',2''-terpyridine (terpy) results in the formation of $[\text{Zn}(\text{terpy})_2](\text{hfac})_2$.

Comment

Previous studies have shown that the reaction of $[\text{Zn}(\text{hfac})_2] \cdot 2\text{H}_2\text{O}$ with *N*-donor heterocyclic ligands produces octahedral metal complexes that contain the $\text{Zn}(\text{hfac})_2$ moiety. Examples of compounds that have been crystallographically characterized are, for monodentate ligands, *cis*- $[\text{Zn}(\text{hfac})_2(\text{pyridine})_2]$ (Pradilla-Sorzano & Fackler, 1973), *trans*- $[\text{Zn}(\text{hfac})_2(\text{py})_2]$, where py is a substituted pyridine (Lee & Wei, 2000), and, for bidentate chelate *N*-heterocyclic ligands, *cis*- $[\text{Zn}(\text{hfac})_2(\text{N}-\text{N})]$, where N-N represents a substituted 2,2'-bipyridine ligand (Kumada *et al.*, 2000; Lee & Wei, 2000; Sakane *et al.*, 2000).



To extend the study to the use of terdentate nitrogen ligands, we have investigated the reaction of $[\text{Zn}(\text{hfac})_2] \cdot 2\text{H}_2\text{O}$, with 2,2':6',2''-terpyridine (terpy), 2,6-bis[1-(4-*tert*-butylphenylimino)ethyl]pyridine (L^1) and 2,6-bis[1-(4-methylphenylimino)ethyl]pyridine (L^2). The product from the reaction with terpy is $[\text{Zn}(\text{terpy})_2](\text{hfac})_2$ which was characterized by elemental analysis and ^1H NMR studies. In $(\text{CD}_3)_2\text{CO}$ solution at 233 K the ^1H NMR spectrum is consistent with the formulation $[\text{Zn}(\text{terpy})_2](\text{hfac})_2$, but at higher temperatures, there is spectral evidence of some intermolecular exchange by virtue of the partial dissociation of the terpy from the zinc and the consequent attachment of the hfac moiety to the metal. In contrast to this, the reaction of $[\text{Zn}(\text{hfac})_2] \cdot 2\text{H}_2\text{O}$ with L^1 or L^2 leads to the isolation of the complexes $[\text{Zn}L_2][\text{Zn}(\text{hfac})_3]_2$ ($L = L^1$ or L^2) which, for $L =$

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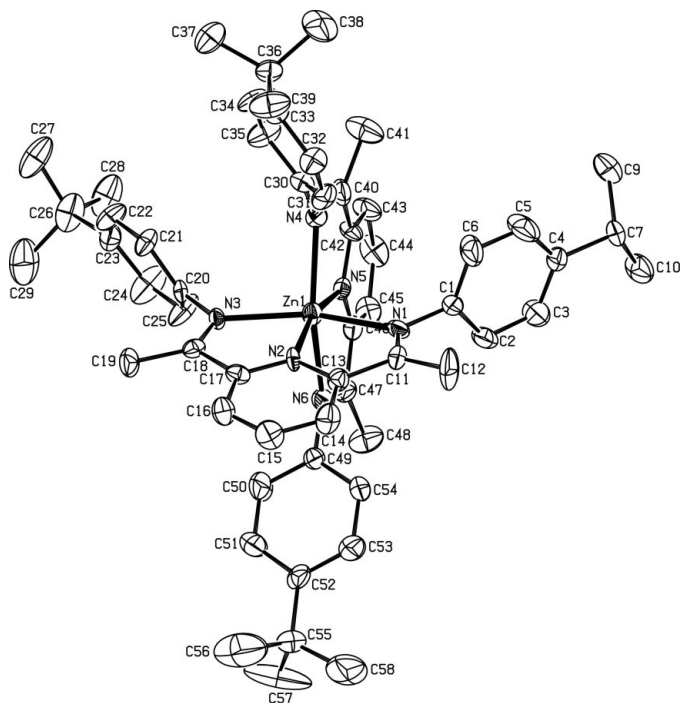


Figure 1
The cation moiety of the title compound (50% probability displacement ellipsoids).

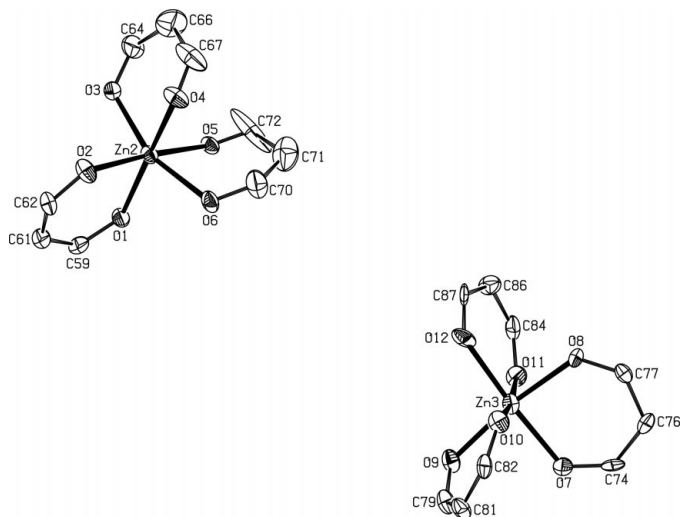


Figure 2
The anion moieties of the title compound (50% probability displacement ellipsoids). The CF_3 groups have been omitted for clarity.

L^1 , is the title compound, (I). The structure of (I) (Fig. 1) shows that all three Zn atoms are octahedrally coordinated. In the cation, Zn1 is coordinated by two *mer*-terdentate chelate L^1 ligands to form a distorted octahedron. For the coordinated L^1 ligands, all the N and C atoms of the ligand skeleton are coplanar (r.m.s. deviations = 0.0507 and 0.0826 for N1/N3- and N4/N6-containing ligands, respectively) with only the substituted phenyl rings being twisted out of the coordination plane (dihedral angles between ligand core and phenyl rings = 85.38, 72.19, 48.86 and 86.74° for rings C1–C6, C20–C25, C30–C35 and C49–C54, respectively). Because of the strain induced in

this type of ligand when it is acting as a terdentate chelate (Edwards *et al.*, 1990), the geometry at Zn1 is a distorted octahedron. The angles N3–Zn1–N1 and N4–Zn1–N6 are reduced from the ideal value of 180° to 149.1 (12) and 150.5 (11)°, respectively. The four $\text{N}_{\text{imino}}\text{—Zn1—N}_{\text{pyridine}}$ bite angles are 76.6 (11), 75.4 (11), 73.9 (11) and 74.0 (11)°, which are much reduced from the expected value of 90°. The bond lengths Zn1– N_{imino} fall in the range 2.15 (3)–2.31 (3) Å, whereas the Zn1– $\text{N}_{\text{pyridine}}$ distances are shorter at 2.03 (3) and 2.06 (3) Å. Similar ligand distortions are observed in the five-coordinate complex ZnCl_2L^3 , where L^3 is 2,6-bis[1-(phenylimino)ethyl]pyridine (Edwards *et al.*, 1990).

The anion moieties of the structure are both composed of three hexafluoroacetylacetonato ligands coordinated octahedrally about a zinc centre with little deformation from idealized geometry. However, these chelating ligands form six-membered rings with the metal centres and have adopted a number of different conformations which have been analysed by puckering analysis (Cremer & Pople, 1975). The chelates around Zn2 form a flat ring (O1–O2 chelate, maximum deviation from mean ring plane = 0.05 Å), an envelope (chelate O3–O4) and a half chair (chelate O5–O6). About Zn3, the rings adopt a flat conformation (O7–O8 chelate, maximum deviation from mean ring plane = 0.027 Å) and envelope conformations for the remaining two ligand ring systems.

Experimental

A solution of $[\text{Zn}(\text{hfac})_2]\cdot 2\text{H}_2\text{O}$ (0.037 g, 0.072 mmol) in diethyl ether was added with stirring to a solution of L^1 (0.020 g, 0.047 mmol) (Granifo *et al.*, 1999) in diethyl ether (10 ml). The yellow solution was concentrated to approximately 5 ml and allowed to stand for 6 h. The yellow crystals obtained were washed with diethyl ether (2×10 ml) and dried under vacuum. Yield 36 mg, 65%. Analysis for $[\text{Zn}(L^1)_2][\text{Zn}(\text{hfac})_3]\cdot 0.5\text{Et}_2\text{O}$, calculated: C 46.75, H 3.67, N 3.56%; found: C 46.34, H 3.40, N 3.68%. The zinc complexes with terpy or L^2 were prepared in a similar fashion. Analyses for $[\text{Zn}(L^2)_2][\text{Zn}(\text{hfac})_3]\cdot 0.5\text{Et}_2\text{O}$, calculated: C 43.03, H 2.47, N 3.96%; found: C 43.06, H 2.47, N 3.89%. Analyses for $[\text{Zn}(\text{terpy})_2](\text{hfac})_2$, calculated: C 50.78, H 2.56, N 8.88%; found: C 50.79, H 2.34, N 8.84%.

Crystal data

$[\text{Zn}(\text{C}_{29}\text{H}_{35}\text{N}_3)_2][\text{Zn}(\text{C}_5\text{HF}_6\text{O}_2)_3]\cdot 0.5\text{C}_4\text{H}_{10}\text{O}$
 $M_r = 2321.68$
 Monoclinic, $C2/c$
 $a = 42.138$ (2) Å
 $b = 19.4444$ (10) Å
 $c = 26.255$ (2) Å
 $\beta = 110.969$ (10)°
 $V = 20088$ (2) Å³
 $Z = 8$

$D_x = 1.535$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 26 256 reflections
 $\theta = 1.8\text{--}25.1^\circ$
 $\mu = 0.84$ mm⁻¹
 $T = 150$ (2) K
 Block, yellow
 $0.35 \times 0.22 \times 0.22$ mm

Data collection

Nonius FAST TV area-detector diffractometer
 φ and ω scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
 $T_{\text{min}} = 0.758$, $T_{\text{max}} = 0.837$
 26 256 measured reflections

14 012 independent reflections
 6038 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.074$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = -47 \rightarrow 49$
 $k = -11 \rightarrow 22$
 $l = -30 \rightarrow 30$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.129$
 $S = 0.76$
 14 012 reflections
 1348 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0364P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 1.002$
 $\Delta\rho_{\max} = 1.04 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.83 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Zn1—N5	2.03 (3)	Zn2—O5	2.07 (3)
Zn1—N2	2.06 (3)	Zn2—O4	2.07 (3)
Zn1—N3	2.15 (3)	Zn2—O6	2.13 (3)
Zn1—N4	2.19 (3)	Zn3—O12	2.03 (3)
Zn1—N1	2.20 (3)	Zn3—O8	2.06 (3)
Zn1—N6	2.31 (3)	Zn3—O7	2.06 (3)
Zn2—O2	2.06 (3)	Zn3—O11	2.07 (3)
Zn2—O3	2.06 (3)	Zn3—O9	2.07 (3)
Zn2—O1	2.07 (3)	Zn3—O10	2.10 (3)
N5—Zn1—N2	165.2 (11)	O1—Zn2—O4	173.2 (11)
N5—Zn1—N3	111.5 (11)	O5—Zn2—O4	98.1 (11)
N2—Zn1—N3	75.4 (11)	O2—Zn2—O6	98.8 (11)
N5—Zn1—N4	76.6 (11)	O3—Zn2—O6	160.3 (10)
N2—Zn1—N4	116.6 (11)	O1—Zn2—O6	94.8 (11)
N3—Zn1—N4	95.4 (11)	O5—Zn2—O6	81.8 (10)
N5—Zn1—N1	99.2 (12)	O4—Zn2—O6	81.5 (12)
N2—Zn1—N1	74.0 (11)	O12—Zn3—O8	87.5 (11)
N3—Zn1—N1	149.1 (12)	O12—Zn3—O7	175.3 (11)
N4—Zn1—N1	95.1 (11)	O8—Zn3—O7	89.2 (11)
N5—Zn1—N6	73.9 (11)	O12—Zn3—O11	86.0 (11)
N2—Zn1—N6	92.9 (11)	O8—Zn3—O11	92.2 (11)
N3—Zn1—N6	94.1 (10)	O7—Zn3—O11	90.8 (11)
N4—Zn1—N6	150.5 (11)	O12—Zn3—O9	99.6 (11)
N1—Zn1—N6	90.9 (11)	O8—Zn3—O9	169.1 (11)
O2—Zn2—O3	95.7 (11)	O7—Zn3—O9	84.0 (11)
O2—Zn2—O1	86.6 (11)	O11—Zn3—O9	96.4 (11)
O3—Zn2—O1	99.3 (11)	O12—Zn3—O10	85.8 (11)
O2—Zn2—O5	173.5 (11)	O8—Zn3—O10	87.1 (11)
O3—Zn2—O5	85.2 (11)	O7—Zn3—O10	97.4 (11)
O1—Zn2—O5	86.9 (11)	O11—Zn3—O10	171.8 (12)
O2—Zn2—O4	88.4 (11)	O9—Zn3—O10	85.3 (11)
O3—Zn2—O4	85.7 (11)		

H atoms were located in idealized positions and their coordinates and displacement parameters allowed to ride on those of the parent atom. The refinement required damping in order to prevent parameters from shifting excessively, due to a low percentage of observed reflections.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989); cell refinement: *MADNES*; data reduction: *MADNES*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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