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Research Article

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Synthesis and Structures of Dimeric Zinc Complexes Supported by Unsymmetrical Rigid Bidentate Imino-acenapthenone Ligand

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Abstract: We report two zinc complexes of molecular formulae $[ZnCl_2(Mes\text{-}BIAO)]_2$ (**3**) and $[ZnCl_2(Dipp\text{-}BIAO)]_2$ (**4**) (Mes = Mesityl, Dipp = 2,6-diisopropylphenyl) of rigid unsymmetrical bidentate iminoacenapthenone ligands (Mes-BIAO) (**1**) and Dipp-BIAO) (**2**). The zinc complexes **3** and **4** can be achieved by the reaction of $ZnCl_2$ and neutral [*N*-(mesityl)-iminoacenapthenone] (**1**) and [*N*-(2,6-diisopropylphenyl)-iminoacenapthenone] ligand (**2**) respectively in dichloromethane at ambient temperature. The solid state structures of the complexes **3** and **4** were established by single crystal X –ray diffraction analysis. In the solid state structures, both the complexes are dimeric in nature. In complexes **3** and **4**, each of the zinc coordination polyhedron is formed by the ligation of imine nitrogen, carbonyl oxygen atoms of the ligand **1** and **2** respectively along with three chlorine atoms. Out these three chlorine atoms, two are μ_2 bridged with adjacent zinc atom to form the dimer. Thus overall zinc atom is penta-coordinated and the geometry can be best described as a distorted trigonal bipyramidal or a distorted square pyramidal.

Keywords: Iminoacenapthenone, Metallacycle, Zinc, Pentacoordinate

1. INTRODUCTION

α-Diimine ligands are known for a long time [1-2] to stabilize various organometallic complexes[3-5]. They can be easily derived from the condensation reaction of a diketone with two equivalents of an alkyl or arylamine often catalyzed by an acid. Using these synthetic routes, we can

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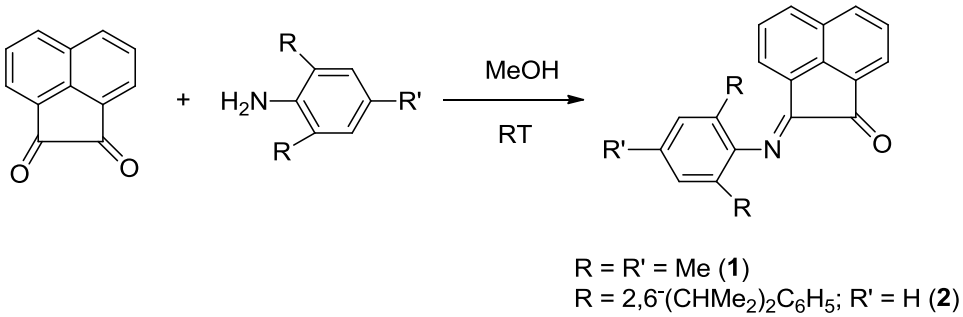

Scheme 1. Synethesis of (**Ar-BIAO**)

easily prepare a wide variety of substituents on the backbone and, thus enabling modification of the steric and electronic effects at the metal center bound to it. The rigid bidentate nitrogen based compounds di-imine ligand bis(*N*-arylimino)acenaphthene (**Ar-BIAN**), was first introduced by van *Asselt* and *Elsevier* in the early 1992 in transition metal chemistry [6]. Since then, they have found widespread use as ligands especially for palladium, ruthenium and nickel and the corresponding complexes have been employed as catalysts for a wide variety of reactions [7-14]. It also accepted that the BIAN derivatives are more rigid compared to diimine ligands derived from glyoxal or related acyclic diketones and this rigidity both imposing the correct geometry for coordination and most of all imparting a high chemical stability both with respect to hydrolysis and rupture of the central C–C bond. The presence of two exocyclic imines to the heteroaromatic ring system lead to better σ-donating and better π-accepting properties than that of 2,2'-bipyridine and 1,10-phenanthroline ligands [15-17]. In addition, the rigid acenaphthene backbone prevents rotation around the imine carbon–carbon bond and forces the imine nitrogen atoms to remain in a fixed *cis* orientation, favoring chelating coordination to a central metal atom [15]. Considering the rigid unsymmetrical imine, carbonyl mixed ligand [*N*-(2,6-diisopropylphenyl)-iminoacenapthenone (Ar-BIAO) which can be obtained as the major product by the single condensation of amine to one of the carbonyl group (Scheme 1) [17,18-20] of the acenaphthenequinone, the situation is quite different. Recently *S. Y. Kim and coworkers* showed that unsymmetrical (Ar-BIAO) nickel complexes can be used as excellent catalyst for the polymerization of propylene [17].

We also reported the synthesis and structural studies of cobalt and copper complexes of ligand **2** to understand the coordination behavior of the unsymmetrical ligand [21]. Due to the presence of one exocyclic carbonyl group in place of second exocyclic imine group, the σ-donating and π-accepting capabilities is reduced in comparison with (**Ar-BIAN**) ligand. The absence of the second 2,6-diisopropylphenyl group also significantly decrease the steric bulk. As a result we observed a penta-coordinated dimeric cobalt complex but only a di-coordinated copper(I) complex where the carbonyl oxygen left apart from coordination to the copper atom. In the continuation of the study to explore the unsymmetrical (Ar-BIAO) ligand, we interested to extend this chemistry to zinc (II) metal to study it's chelating behavior. Recently *Dagorne* and *Avilés* and coworkers reported that BIAN supported zinc alkyl cations are found as highly active catalyst in the immortal ring opening polymerization of ε-caprolactone to yield narrowly disperse and chain length-controlled poly(ε-caprolactone)[22]. BIAN supported zinc complexes are also utilized by *Ragaini* and coworkers to probe the stability of the complexes by introducing various strain into the rigid bidentate BIAN ligands [23]. Filgueiras and Bordinhao and coworkers reported various zinc complexes supported by Ar-BIAN ligands and chlorides and

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thiocyanides as co-ligands [24]. Herewith we present the full accounts of syntheses and structural studies of two zinc complexes $[ZnCl_2(Mes\text{-}BIAO)]_2$ (**3**) and $[ZnCl_2(Dipp\text{-}BIAO)]_2$ (**4**) with two different Ar-BIAO ligands **1** and **2** respectively.

2. Experimental

2.1. General Information

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glove box. Dichloromethane and petroleum ether are dried over P_2O_5 followed by distillation and kept under molecular sieves prior to use. ^1H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Ligand **1**, **2** were prepared according to the literature method [20,21] and anhydrous $ZnCl_2$ was purchased from Sigma Aldrich and used as such.

2.2 Synthesis of $[ZnCl_2(Mes\text{-}BIAO)]_2$ (3)

In a dry degassed Schlenk tube, ligand **1** (100 mg, 0.3 mmol) was taken and 10 mL of CH_2Cl_2 was added and to this mixture anhydrous $ZnCl_2$ (45.5mg, 0.3mmol) was added under inert atmosphere. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered using cannula filtration. The colour of the filtrate was deep reddish-orange. The CH_2Cl_2 was evaporated under *vacuo* to result a concentrated clear solution which was subjected to crystallization at -40^0C. Single crystals of light orange colour were obtained after re-crystallization from dichloromethane. Yield: 135 mg, 93%, m.p. 175^o C.
FT- IR (selected frequency): ν = 2962, 2920, 2854, 1727(C=O), 1649(C=N), 1588, 1435, 1258, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, 1H, An *H*), 8.16 (t, 1H, An *H*), 7.94 (t, 1H, An *H*), 7.59 (t, 1H, An *H*), 7.03 (d, 1H , An *H*), 6.93 (d, 2H, Ar *H*), 6.88 (d, 1H, An *H*) 2.38 (d, 3H, ^3J = 3.76 Hz, *p*-CH_3), 2.15 (s, 6H, *o*-C*H*$_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, selected resonances): δ =189.8 (*C*=O), 164.2 (*C*=N), 140.2, 137.2, 132.6, 132.4, 130.9, 130.9, 129.9, 129.6, 129.3, 129.0, 128.4, 128.3,125.8, 125.5, 122.0, 20.5(*o*-*C*H$_3$), 18.2(*p*-*C*H$_3$). Anal. Calcd. for $C_{46}H_{42}Cl_{12}N_2O_2Zn_2$ (1211.03), C 45.62, H 3.50, N 2.31. Found, C 45.17, H 3.15, N 2.21.

2.3 Synthesis of $[ZnCl_2(Dipp\text{-}BIAO)]_2$ (4)

In a dry degassed Schlenk tube, 2 (125 mg, 0.37 mmol) was taken and about 6 mL of CH_2Cl_2 was added onto it. To this solution mixture, anhydrous $ZnCl_2$ (50 mg, 0.37 mmol) was added. The reaction mixture was stirred for 6 h at ambient temperature. This reaction mixture was filtered using cannula filtration. The colour of the filtrate was deep orange in colour. The CH_2Cl_2 was evaporated under *vacuo* resulting in a concentrated clear solution which was subjected to crystallization at -40^0C. Single crystals of light orange colour were obtained after second re-crystallization. Yield: 140 mg (80%).
FT- IR (selected frequency): ν = 3063, 2962, 2926, 1729 (C=O), 1651(C=N), 1588, 1434, 1273, 779, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (t, 2H, An *H*), 8.11 (d, 1H, An *H*), 7.91 (t, 1H, An *H*), 7.48 (t, 1H, An *H*), 7.34(m, 1H, Ar *H*) 7.27 (d, 2H , Ar *H*), 6.65 (d, 1H, An *H*), 2.90 (sept, 2H, C*H*(CH3)$_2$), 1.19, (d, 6H, CH(C*H*$_3$)$_2$), 0.76 (d, 6H, CH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, selected resonances): δ = 189.32 (*C*=O), 161.61 (*C*=N), 137.2, 133.8, 131.0, 129.9, 128.3, 127.7, 126.7, 124.7, 123.9, 123.7, 123.6, 27.6 (*C*H(CH$_3$)$_2$), 23.4, 23.0 (CH(*C*H$_3$)$_2$). Anal. Calcd. for $C_{50}H_{50}Cl_8N_2O_2Zn_2$ (1125.33), C 53.37, H 4.48, N 2.49. Found, C 52.97, H 4.23, N 2.29.

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Table 1. Crystallographic structural refinement parameters of $[ZnCl_2(Mes\text{-}BIAO)]_2$ (**3**) and $[ZnCl_2(Dipp\text{-}BIAO)]_2$ (**4**).

	3.2(CH_2Cl_2)	**4.(CH_2Cl_2)**
CCDC No.	931501	931500
Empirical Formula	$C_{46}H_{42}Cl_{12}N_2O_2Zn_2$	$C_{50}H_{50}Cl_8N_2O_2Zn_2$
FormulaWt	1211.00	1125.26
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P* 2_1/c
a, [Å]	10.5547(9)	12.0406(13)
b, [Å]	11.0295(10)	13.1834(7)
c, [Å]	11.6257(10)	19.4514(13)
α, [°]	103.902(8)	90
β, [°]	101.519(7)	122.564(5)
g, [°]	92.896(7)	90
V, [Å ^{3}]	1280.36(19)	2602.2(4)
Z	1	2
Density (mg/m^3)	1.571	1.436
T, K	150(2)	150(2)
Radiation	CuKα (λ = 1.54184Å)	CuKα (λ = 1.54184Å)
μ, mm^{-1}	5.225	7.231
Θ range for data collection[°]	4.01 to 70.71	4.30 to 70.96
Absorption correction	Multi-scan	Multi-scan
Reflections collected	9066	11153
Unique reflections	4809 [R_{int} =0.0445]]	4932 [R_{int} = 0.0335
Completeness to Θ	97.7%	98.3%
Datta/restrant /parameter	4809/0/292	4932/0/293
R_1; wR_2	0.0947; 0.1996	0.0657; 0.1653
GOOF	1.034	1.069

2.4. Single-Crystal X-Ray Structure Determinations

Single crystals of compound **3** and **4** were grown from a solution of CH_2Cl_2 under argon atmosphere at a temperature of - 40°C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on a Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic CuKα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in the Table 1. The structures were solved by direct methods (SIR92) [25] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97 [26]. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their

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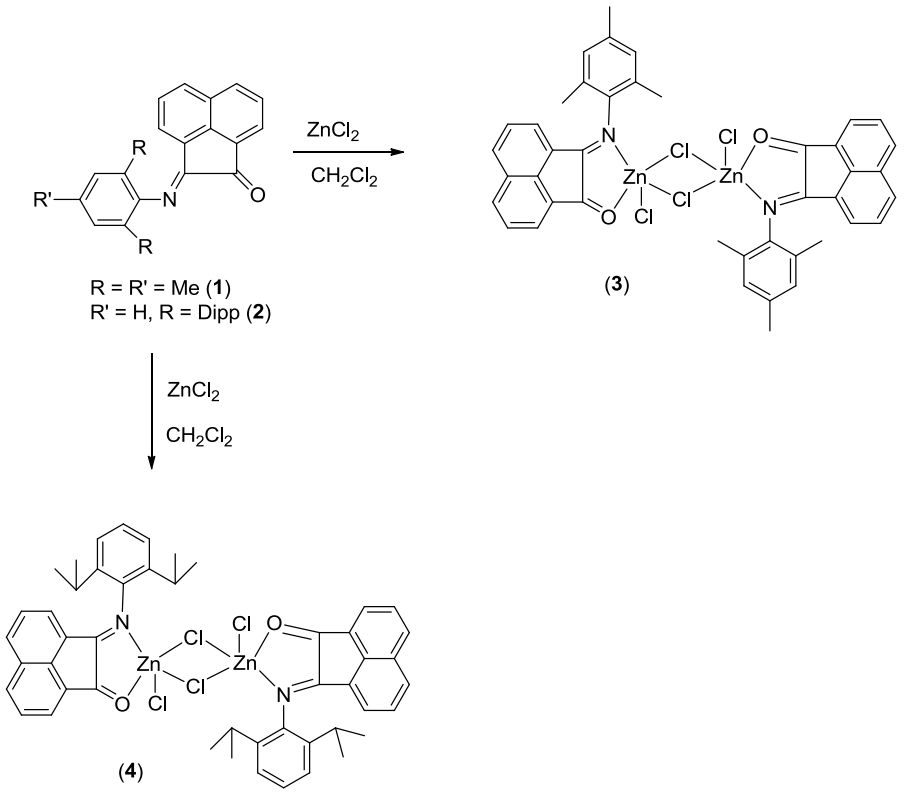
carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 931500 (**4**), 931501 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

3. RESULTS AND DISCUSSION

To a suspension of anhydrous Zn(II) chloride in dichloromethane, solution of ligand **1** was added drop wise in a 1:1 molar ratio, an immediate color changes from red to brown was noticed. The reaction mixture was stirred for overnight at room temperature for another 12 h. The reaction solution was filtered under inert atmosphere and then washed with dry petroleum ether. The title compound $[ZnCl_2(Mes\text{-}BIAO)]_2$ (**3**) was re-crystallized from dichloromethane (Scheme 2). In a similar fashion other zinc complex $[ZnCl_2(Dipp\text{-}BIAO)]_2$ (**4**) was obtained when the anhydrous zinc chloride was treated with ligand **2** in dichloromethane solution (Scheme 2) at ambient temperature. Both the complexes were characterized by spectroscopic techniques and combustion analysis. The solid state structures of both the complexes were characterized by single crystal X-ray diffraction analysis.



Scheme 2. Syntheses of zinc complexes of **3** and **4**.

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In FT-IR spectra of the compounds **3** and **4** show strong absorption at 1727 cm^{-1} and 1729 cm^{-1} respectively for the C=O stretching, and the absorption at 1649 (**3**) and 1651 (for **4**) cm^{-1} can be assigned for C=N bond stretching of the iminoacenapthenone moieties. The C=N stretching frequencies are in the agreement with our previous observation and also with reported values (1688 and 1636 cm^{-1}).[13, 24] ^{1}H NMR spectra of the compounds **3** and **4** measured in $CDCl_3$, reveal only one set of signals for each complex due to the dynamic behavior of the each compounds. In the ^{1}H NMR spectra of **3**, the doublet peak at 2.38 ppm along with a coupling constant of 3.76 Hz can be assigned for the three methyl protons at *p*-position of the mesityl group, whereas the sharp singlet at 2.15 ppm are due to the resonance of six methyl protons located at 2,6 position of the mesityl group of ligand **1** and this is slightly high field shifted compare to that of free ligand (2.01 ppm). The resonances of the protons of acenapthene back bone are in the expected region and in well agreement with the free ligand **1** [20]. For another zinc complex **4**, in the ^{1}H spectra two doublets are obtained at δ = 1.19 ppm (*J* = 6.68 Hz) and 0.76 (*J* = 6.88 Hz) ppm in 1:1 ratio and can be assigned as the methyl protons attached to isopropyl groups on the aromatic ring. The septet at δ = 2.90 ppm which is slightly down field shifted compared to that of **2** (2.8 ppm) [21] corresponds to the resonance of the CH proton present in the isopropyl groups. The resonances for the protons attached to the acenapthene moiety and the phenyl ring are in the expected regions. In ^{13}C{^{1}H} NMR spectra of the compound **4**, carbonyl carbon is mostly de-shielded and appears at δ = 189.3 ppm, then imine carbon at 161.1 ppm, and phenyl carbon attached to nitrogen atom at 142.5 ppm which is slightly high field shifted upon coordination with zinc [21].

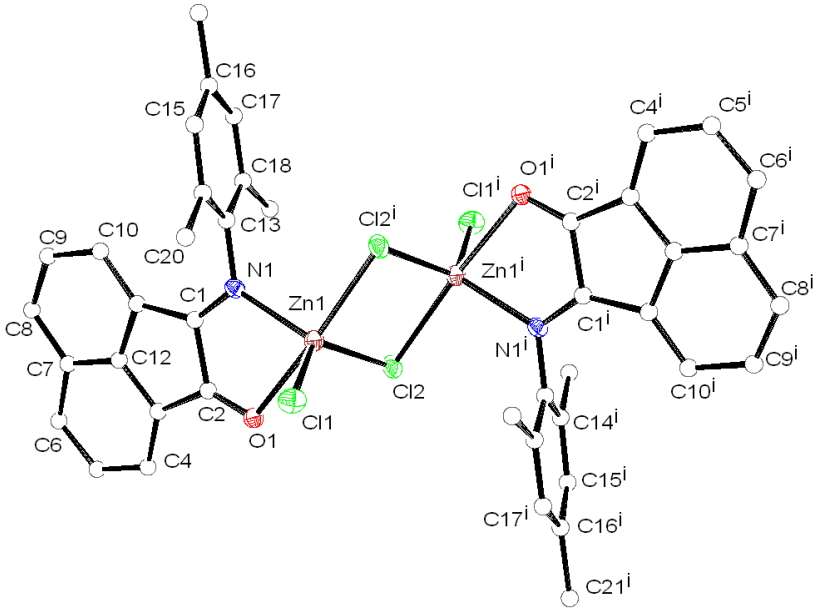

Figure 1. Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms atoms for clarity. Selected distances [Å] and angles [^{o}] Selected bond lengths (Å) Zn(1)-N(1) 2.106(5), Zn(1)-Cl(1) 2.2089(17), Zn(1)-Cl(2) 2.3251(17), Zn(1)-O(1) 2.410(4), Zn(1)-Cl(2)^i 2.4177(16), O(1)-C(2) 1.211(7), N(1)-C(1) 1.289(7), N(1)-Zn(1)-Cl(1) 113.92(14), N(1)-Zn(1)-Cl(2) 116.74(14), Cl(1)-Zn(1)-Cl(2) 123.86(7), N(1)-Zn(1)-O(1) 75.71(16), Cl(1)-Zn(1)-O(1) 87.82(11), Cl(2)-Zn(1)-O(1) 82.61(11), N(1)-Zn(1)-Cl(2)^i 96.62(13), Cl(1)-Zn(1)-Cl(2)^i 107.49(7), Cl(2)-Zn(1)-Cl(2)^i 89.29(6), O(1)-Zn(1)-Cl(2)^i 164.66(11), C(2)-O(1)-Zn(1) 107.5(4), C(1)-N(1)-Zn(1) 117.1(4), C(13)-N(1)-Zn(1) 123.7(4)

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Table 2. Selected Bond Lengths (Å) and Angles (°) of $[ZnCl_2(Mes\text{-}BIAO)]_2$ (**3**) and $[ZnCl_2(Dipp\text{-}BIAO)]_2$ (**4**).

Bond Lengths (Å)	**3**	**4**
Zn(1)-N(1)	2.106(5)	2.073(3)
Zn(1)-Cl(1)	2.2089(17)	2.2025(11)
Zn(1)-Cl(2)	2.3251(17)	2.4421(10)
Zn(1)-O(1)	2.410(4)	2.513(2)
Zn(1)-Cl(2)^{i}	2.4177(16)	2.2769(10)
O(1)-C(2)	1.211(7)	-
N(1)-C(1)	1.289(7)	-
Bond Angle (°)		
N(1)-Zn(1)-Cl(1)	113.92(14)	111.02(9)
N(1)-Zn(1)-Cl(2)	116.74(14)	96.51(8)
Cl(1)-Zn(1)-Cl(2)	123.86(7)	106.49(4)
N(1)-Zn(1)-O(1)	75.71(16)	-
Cl(1)-Zn(1)-O(1)	87.82(11)	-
Cl(2)-Zn(1)-O(1)	82.61(11)	-
N(1)-Zn(1)-Cl(2)^{i}	96.62(13)	125.08(9)
Cl(1)-Zn(1)-Cl(2)^{i}	107.49(7)	118.75(4)
Cl(2)-Zn(1)-Cl(2)^{i}	89.29(6)	90.68(3)
O(1)-Zn(1)-Cl(2)^{i}	164.66(11)	--------
C(2)-O(1)-Zn(1)	107.5(4)	--------
C(1)-N(1)-Zn(1)	117.1(4)	--------
C(13)-N(1)-Zn(1)	123.7(4)	--------

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The solid state structures of the compounds **3** and **4** were established by single crystal X-ray diffraction analysis and the structural refinement parameters are given in the Table 1. A comparative study of bond lengths and bond angles are given in Table 2. The compound **3** crystallizes in triclinic space group *P-1* having one molecule of **3** and two molecules of dichloromethane in the unit cell. In contrast the complex **4** crystallizes in monoclinic space group *P* 2_1/c having two molecules of **4** and one molecule of dichloromethane in the unit cell. Both the zinc complexes **3** and **4** are dimeric and two zinc atoms are bridged through two chlorine atoms (Fig 1 for **3** and Fig 2 for **4**). Both the zinc complexes are centrosymmetric due the presence of an inversion center in the middle of each of the molecule. In **3**, two five member zinc metallacycles Zn1-O1-C2-C1-N1 and $Zn1^i$-$O1^i$-$C2^i$-$C1^i$-$N1^i$ are formed by the two imino acenathenone ligand **1** moieties and two zinc atoms. Each zinc atom is chelated through the lone pairs located on neutral carbonyl oxygen and the imine nitrogen atoms. In the similar fashion, each of the zinc coordination polyhedron in **4** is formed by the ligation of imine nitrogen, carbonyl oxygen atoms of the ligand **2** along with three chlorine atoms.

In both the complexes, the geometry around each zinc atom can be best described either a distorted square pyramidal having N1, O1, Cl2, $Cl2^i$ atoms for **3**, (N1, O1, Cl2, $Cl2^i$ for **4**) in the basal position and Cl1 in the axial position (Cl1 for **4**) or distorted trigonal bipyramidal having N1 Cl1 Cl2 atoms (for **3**) are in the equatorial position (N1 Cl1 Cl2 for **4**) and O1, $Cl2^i$ atoms are in the axial position (O1, $Cl2^i$ for **4**). Thus compound **3** and **4** is an example of having unusual penta coordinated zinc atom. It is noteworthy that by using Ar-BIAN ligands, the corresponding zinc complexes (Ar-BIAN-$ZnCl_2$) and dimeric [Ar-BIAN-$Zn(CNS)_2]_2$ [24] contain tetrahedral geometry around the zinc center. Thus penta coordinated zinc complexes **3** and **4** are rare in literature [27, 28]. Zn-O distance 2.410(4) Å (2.513(2) for **4**) which is well agreement with the Zinc oxygen coordination bond rather covalent bond (Zn-O 1.976 (2) Å for covalent bond [29]. The slight elongation of Zn-O bond in **4** compare to that in **3**, can be attributed due to steric crowding of the two isopropyl groups at 2,6 position in ligand **2** moieties. The Zn1-N1 2.1062(5) Å (for 3) and 2.073(3) Å (for **4**) are in the range of the zinc nitrogen coordination bond as the similar Zn-N distance 2.023(3) -2.34(3) Å is observed for Zn(mmpcd)]ClO_4 (mmpcd = $Me_2pzCH_2)_2NC_2H_3MeNHC_5H_6CSSCH_3$) (pz = pyrazole) reported by *Chaudhury et al*. [28] and 1.994(2) - 2.050(2) Å observed for [{$CH(Ph_2PNSiMe_3)_2$}$ZnN(SiMe_3)_2$] reported by *Roesky et al*. [30] In each of the zinc complexes **3** and **4**, the three different Zn-Cl distances Zn-Cl1 2.209(2) (for **3**), 2.203(1) (for **4**), Zn1-Cl2 2.325(2) (for **3**), 2.277(1) (for **4**) and Zn1-$Cl2^i$ 2.418(2) (for **3**), 2.442(1) Å (for **4**) indicating an asymmetric attachment of the chlorine atoms to the zinc center. One chlorine (Cl1) atom is purely covalent bonded, whereas Cl2 is bonded covalntly as well as bridging mode which elongate Zn-Cl distance little bit 2.325(2), and the third chlorine atom ($Cl(2^i)$ is purely coordination bond and having the longest Zn-Cl distance 2.418(2) Å. Identical situation is observed for the second zinc atom as well. The C-O bond distance 1.228(7) Å (for **3**) and 1.225(5) Å (for **4**), and the C-N distance 1.292(7) Å (for **3**), 1.280(4) Å (for **4**) in are similar and unpurturbed compare to that of the respective ligands. [20,21] The distance between two zinc atoms of 3.375 Å (for **3**) and 3.319 Å (for **4**) suggests no interaction between two zinc atoms present in the complex. In **3**, each zinc atom is placed 0.025 Å above the plane containing acenapthene and the donor oxygen and nitrogen atoms. The dihedral angle between the acenapthene plane and the plane containing N, O and Zn atoms is 2.14^o indicating N, O, Zn atoms are almost coplaner with the acenapthene plane. However, the mesityl phenyl ring on the nitrogen atoms make 76.76^o of dihedral angle with the acenapthene plane containing nitrogen and oxygen atoms as well. In contrast, each zinc atom in complex **4**, resides 0.474 Å above the plane containing acenapthene and the donor oxygen and nitrogen atoms. The acenapthene plane and the plane containing N, O and Zn atoms makes a dihedral

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angle of 15.88° indicating N, O, Zn atoms have been deviated from coplanarity with the acenapthene plane. This deviation can be due to the presence of two bulky isopropyl groups of the disopropylphenyl moieties.

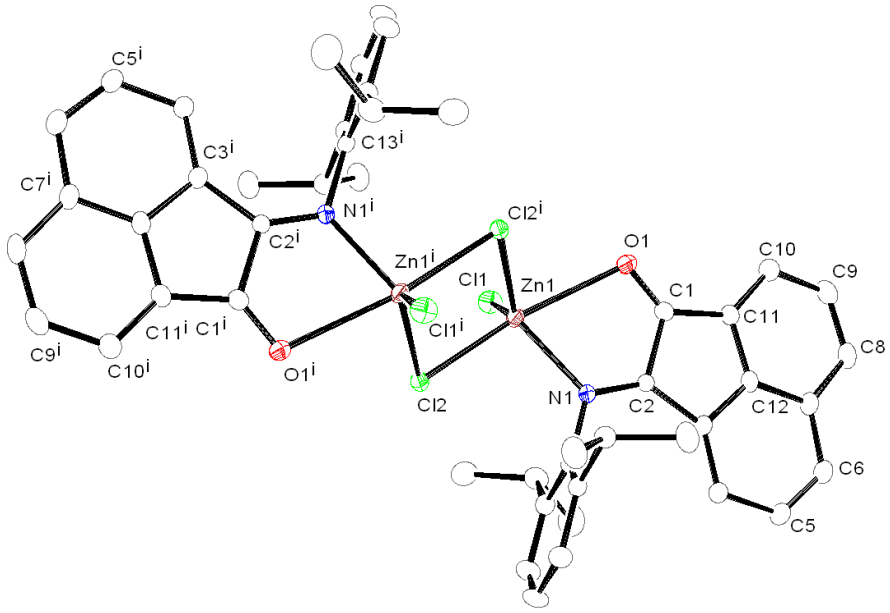

Figure 2. Solid-state structure of **4** showing the atom labeling scheme, omitting hydrogen atoms for clarity. Selected distances [Å] and angles [°] Zn(1)-N(1) 2.073(3), Zn(1)-Cl(1) 2.2025(11), Zn(1)-Cl(2)^{i} 2.2769(10), Zn(1)-Cl(2) 2.4421(10), Cl(2)-Zn(1)^{i} 2.2769(10), N(1)-Zn(1)-Cl(1) 111.02(9), N(1)-Zn(1)-Cl(2)^{i} 125.08(9), Cl(1)-Zn(1)-Cl(2)^{i} 118.75(4), N(1)-Zn(1)-Cl(2) 96.51(8), Cl(1)-Zn(1)-Cl(2) 106.49(4) Cl(2)^{i}-Zn(1)-Cl(2) 90.68(3), Zn(1)^{i}-Cl(2)-Zn(1) 89.32(3), C(2)-N(1)-Zn(1) 118.7(2), C(13)-N(1)-Zn(1) 122.2(2).

4. CONCLUSION

In summary, we have reported two penta coordinated dimeric zinc complexes supported by rigid unsymmetrical bidentate iminoacenapthenone ligands **1** and **2**. Both the complexes can be described as distorted square pyramidal or distorted trigonal bipyramidal geometry. Both the zinc complexes are potentially active for polymerization of ethylene and further studies are in progress in our working group.

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