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Syntheses and solid state structures of zinc (II) complexes with Bi-dentate *N*-(Aryl)imino-acenapthenone (Ar-BIAO) ligands

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Abstract. We have synthesized five zinc complexes of molecular formulae [$ZnCl_2$(2,6-dimethylphenyl-BIAO)]$_2$ (**1a**), [$ZnBr_2$(2,6-dimethylphenyl-BIAO)]$_2$ (**1b**), [ZnI_2(2,6-dimethylphenyl-BIAO)]$_2$(**1c**), [$ZnBr_2$(mes-BIAO)]$_2$(**2b**) and [$ZnBr_2$(dipp-BIAO)] (**3b**) with rigid unsymmetrical iminoacenaphthenone ligands, (2,6-dimethylphenyl-BIAO) (**1**), (mesityl-BIAO) (**2**) and (2,6-diisopropylphenyl-BIAO) (**3**). The zinc complex **1a** was prepared by the reaction of $ZnCl_2$ and neutral (mesityl-BIAO) (**1**). However, complexes **1b**, **2b** and **3b** were obtained by the treatment of $ZnBr_2$ and neutral ligands **1**–**3** respectively in 1:1 molar ratio in dichloromethane at ambient temperature. In a similar reaction of ZnI_2 with (2,6-dimethylphenyl-BIAO) (**1**) in dichloromethane the corresponding iodo-complex **1c** was obtained in good yield. All the zinc (II) complexes are characterized by FT-IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopic techniques. The solid state structures of the complexes **1a**, **1b**, **1c**, **2b** and **3b** are confirmed by single crystal X-ray diffraction analysis. The molecular structures of complexes **1a**, **1b**, **1c** and **2b** reveal the dimeric nature of the complexes and subsequently the centre atom zinc is penta-coordinated to adopt distorted trigonal bipyramidal geometry around it. In contrast, the complex **3b** is in monomeric in nature due to bulkier size of the ligand and zinc ion is tetra coordinated to adopt distorted tetrahedral geometry.

Keywords. Zinc(II); iminoacenathenone; penta- and tetra- coordinated; metallacycle; chelating ligands; steric crowding

1. Introduction

Zinc (II) complexes have been widely studied by several research groups for the past decades. The growing interest in the development of zinc catalysts for lactide polymerization[1–9] is one of the driving force. Recently N Zhao *et al.* have successfully reported some tridentate [NO] based ligands and their Zn(II), Ta(IV), Ti(IV), Zr(IV) complexes along with lanthanides, which are implemented as useful catalysts for a range of organic transformations.[10–16] As an alternative method, by switching the ligand systems from tridentate to bidentate nature, tuning of catalytic activity of the metal complexes can be anticipated. Clearly, most of the applied metals (e.g., Pd, Rh, Ru, Ir) displayed difficulties by their low abundance, high price or toxicity. But zinc complexes are less toxic, has high abundance and low price. On the basis of that, research groups are now focusing on different zinc complexes for catalytic activity in organic transformations. V Bette *et al.* have already reported the reduction of alkyl and aryl carbonyl by using zinc complex as a catalyst using Polymethylhydrosiloxane (PMHS).[17] Besides the reduction of carbonyl, zinc complexes can also catalyze hydrosilylation and exhibit polymerization of olefins. In recent years, we have developed a series of rigid bi-dentate [NO]-based *N*-(aryl) imino-acenapthenone (Ar-BIAO) ligands.[18] This class of ligands can be obtained from the single condensation of acenaphthequinone and aryl amine moiety in 1:1 ratio in acidic medium (scheme 1) as a major product. In comparison with doubly condensed product (Ar-BIAN) first introduced by van Asselt and Elsevier,[19] the Ar-BIAO ligand contains conjugated exocyclic carbonyl and imine groups. Secondly, the rigidity of the acenaphthene backbone forces the imine N-atoms to remain in a fixed *cis* orientation with the exocyclic carbonyl group which favours the chelating coordination to a metal centre. Similar to Ar-BIAN, 2,2′-bipyridine and 1,10-phenanthroline ligands,[20–22] the σ-donating and π-accepting properties of the Ar-BIAO ligands are observed due to the presence of exocyclic carbonyl and exocyclic imine groups

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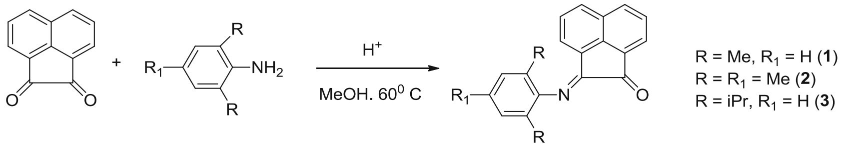


Scheme 1. Synthesis of (Ar-BIAO).

attached with rigid acenaphthene backbone. Herein, we present the full accounts of the synthesis and structural studies of five zinc complexes with Ar-BIAO ligands, $[ZnCl_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**1a**), $[ZnBr_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**1b**), $[ZnI_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**1c**), $[ZnBr_2(\text{mes-BIAO})]_2$ (**2b**) and $[ZnBr_2(\text{dipp-BIAO})]$ (**3b**) and their UV-vis spectroscopic properties in solution and in solid state.

2. Experimental

2.1 *General Information*

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled glove box. Dichloromethane and pentane were dried by standard methods and kept under molecular sieves prior to use. ^{1}H NMR (400 MHz) and ^{13}C {^{1}H} 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. Ar-BIAO ligands **1-3** were prepared according to the literature method[18,23] and anhydrous $ZnCl_2$, $ZnBr_2$ and ZnI_2 were purchased from Sigma Aldrich and used without further purification.

2.2 *Synthesis of $[ZnCl_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (1a)*

In a dry degassed Schlenk tube, ligand **1** (200 mg, 0.70 mmol) was placed and about 10 mL of CH_2Cl_2 was added on to it. The solution was charged with anhydrous $ZnCl_2$ (96 mg, 0.70 mmol) at ambient temperature under inert atmosphere. The reaction mixture was stirred for another 12 h and then the reaction mixture was filtered using cannula filtration. Deep reddish-orange coloured filtrate was evaporated to dryness under *vacuo*. The residue was re-dissolved in 2 mL chloroform and pentane (2 mL) was layered on to it and kept for crystallization at −40°C. Single crystals of light orange colour were obtained after 2–3 days. Yield: 239 mg (81%). FT-IR (selected frequency): $\nu = 3057$ (Ar-*H*), 2918 (C-*H*), 2854 (C-*H*), 1725 (C=O), 1645 (C=N), 1584, 1420, 1280, 1221, 840, 785 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.38 (t, 2H, An-*H*), 8.21 (t, 1H, An-*H*), 7.96 (t, 1H, An-*H*), 7.56 (t, 1H, An-*H*), 7.19 (m, 3H, Ar-*H*), 6.78 (d, 1H, An-*H*), 2.21 (s, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ 189.3 (C=O), 161.2 (C=N), 147.4 (Ar-C), 140.9 (Ar-C), 135.0 (Ar-C), 132.1 (Ar-C), 130.0 (Ar-C), 128.8 (Ar-C), 128.4 (Ar-C), 127.4 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 126.8 (Ar-C), 126.5 (Ar-C), 125.4 (Ar-C), 124.6 (Ar-C), 122.6 (Ar-C), 19.7 (CH_3) ppm. Elemental analysis: ($C_{42}H_{32}Cl_{10}N_2O_2Zn_2$) (**1a.**$CHCl_3$) Calc. C 46.62, H 2.98, N 2.59; found C 46.22, H 2.61, N 2.33.

2.3 *Synthesis of $[ZnBr_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (1b)*

In a dry degassed Schlenk tube, ligand **1** (200 mg, 0.70 mmol) was placed and about 10 mL of CH_2Cl_2 was added on to it. The solution was charged with anhydrous $ZnBr_2$ (158 mg, 0.70 mmol) at ambient temperature under inert atmosphere. The reaction mixture was stirred for another 12 h and then the reaction mixture was filtered using cannula filtration. Deep reddish-orange coloured filtrate was concentrated to 2 mL and pentane (2 mL) was layered on to it and kept for crystallization at −40°C. Single crystals of light orange colour were obtained after 2–3 days. Yield: 271 mg (76%). FT-IR (selected frequency): $\nu = 3065$, 2919, 2851, 1726 (C=O), 1650 (C=N), 1587, 1434, 1280, 1221, 777, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.47 (t, 2H, An-*H*), 8.27 (d, 1H, An-*H*), 8.05 (dd, 1H, An-*H*), 7.65 (dd, 1H, An-*H*), 7.30 (m, 3H, Ar-*H*), 6.86 (d, 1H, An-*H*), 2.29 (s, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 190.7 (C=O), 162.7 (C=N), 147.8 (Ar-C), 142.2 (Ar-C), 135.8 (Ar-C), 133.0 (Ar-C), 132.6 (Ar-C), 130.9 (Ar-C), 129.7 (Ar-C), 129.5 (Ar-C), 129.3 (Ar-C), 128.4 (Ar-C), 128.1 (Ar-C), 128.0 (Ar-C), 127.8 (Ar-C), 127.5 (Ar-C), 127.0 (Ar-C), 126.6 (Ar-C), 125.6 (Ar-C), 123.7 (Ar-C), 18.9 (CH_3) ppm. Elemental analysis: ($C_{44}H_{40}Br_4Cl_8N_2O_2Zn_2$) (**1b.**$2CH_2Cl_2$) Calc. C 38.78, H 2.96, N 2.06; found C 38.53 H 2.59, N 1.89.

2.4 *Synthesis of [ZnI$_2$(2,6-dimethylphenyl-BIAO)]$_2$ (**1c**)*

In a dry degassed Schlenk tube, ligand **1** (200 mg, 0.70 mmol) was placed and about 10 mL of CH_2Cl_2 was added on to it. The solution was charged with anhydrous ZnI_2 (224 mg, 0.70 mmol) at ambient temperature under inert atmosphere. The reaction mixture was stirred for another 12 h and then the reaction mixture was filtered using cannula filtration. Deep reddish-orange coloured filtrate was concentrated to 2 mL and pentane (2 mL) was layered on to it and kept for crystallization at −40°C. Single crystals of light orange colour were obtained after 2–3 days. Yield: 355 mg, 84%. FT-IR (selected frequency): $\nu = 3053$, 2918, 2850, 1705 (C=O), 1645 (C=N), 1584, 1420, 1288, 1221, 833, 775 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 8.48$ (q, 2H, An-H), 8.28 (d, 1H, An-H), 8.05 (t, 1H, An-H), 7.65 (t, 1H, An-H), 7.29 (m, 3H, Ar-H), 6.87 (d, 1H, An-H), 2.36 (s, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ 189.7 (C=O), 161.7 (C=N), 147.1 (Ar-C), 140.9 (Ar-C), 135.0 (Ar-C), 132.1 (Ar-C), 130.0 (Ar-C), 128.8 (Ar-C), 128.4 (Ar-C), 127.4 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 126.8 (Ar-C), 126.5 (Ar-C), 126.3 (Ar-C), 125.4 (Ar-C), 124.6 (Ar-C), 122.6 (Ar-C), 19.7 (CH_3) ppm. Elemental analysis: ($C_{42}H_{34}Cl_4I_4N_2O_2Zn_2$) (**1c.**$CH_2Cl_2$) Calc. C 36.58, H 2.49, N 2.03; found C 35.98, H 2.13, N 1.85.

2.5 *Synthesis of [ZnBr$_2$(Mes-BIAO)]$_2$ (**2b**)*

In a dry degassed Schlenk tube, ligand **2** (200 mg, 0.67 mmol) was placed and about 10 mL of CH_2Cl_2 was added on to it. The solution was charged with anhydrous $ZnBr_2$ (150 mg, 0.67 mmol) at ambient temperature under inert atmosphere. The reaction mixture was stirred for another 12 h and the reaction mixture was filtered using cannula filtration. Deep reddish-orange coloured filtrate was concentrated to 2 mL and pentane (2 mL) was layered on to it and kept for crystallization at −40°C. Single crystals of light orange colour were obtained after 2–3 days. Yield: 280 mg 80%. FT-IR (selected frequency): $\nu = 2920$, 2851, 1729 (C=O), 1648 (C=N), 1587, 1435, 1290, 1224, 779, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$ 25°C): δ 8.46 (q, 2H, An-H), 8.28 (d, 1H, An-H), 8.03 (d, 1H, An-H), 7.60 (q, 1H, An-H), 6.96 (d, 1H, An-H), 6.91 (d, 2H, Ar-H), 2.40 (s,3H, p-CH_3), 2.34 (s, 3H, o-CH_3), 2.25 (s, 3H, o-CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ 190.1 (C=O), 164.32 (C=N), 140.2 (Ar-C), 138.1 (Ar-C), 137.3 (Ar-C), 136.0 (Ar-C), 133.1 (Ar-C), 132.4 (Ar-C), 130.9 (Ar-C), 130.0 (Ar-C), 129.7 (Ar-C), 129.6 (Ar-C), 129.3 (Ar-C), 128.3 (Ar-C), 127.1 (Ar-C), 126.4 (Ar-C), 125.8, (Ar-C) 125.7 (Ar-C), 125.6 (Ar-C), 21.0 (CH_3), 18.9 (CH_3) ppm. Elemental analysis: ($C_{46}H_{42}Br_4Cl_8N_2O_2Zn_2$) (**2b.**$2CH_2Cl_2$) Calc. C 39.78, H 3.05, N 2.02; found C 39.31, H 2.79, N 1.89.

2.6 *Synthesis of [ZnBr$_2$(Dipp-BIAO)] (**3b**)*

In a dry degassed Schlenk tube, ligand **3** (200 mg, 0.58 mmol) was placed and about 10 mL of CH_2Cl_2 was added on to it. The solution was charged with anhydrous $ZnBr_2$ (132 mg, 0.58 mmol) at ambient temperature under inert atmosphere. The reaction mixture was stirred for another 12 h and then the reaction mixture was filtered using cannula filtration. Deep reddish-orange coloured filtrate was concentrated to 2 mL and pentane (2 mL) was layered on to it and kept for crystallization at −40°C. Single crystals of light orange colour were obtained after 2–3 days. Yield: 259 mg 78%. FT-IR (selected frequency): $\nu = 3063$, 2963, 2927, 1726 (C=O), 1649 (C=N), 1586, 1434, 1274, 778, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.40 (t, 2H, An-H), 8.21 (d, 1H, An-H), 7.98 (t, 1H, An-H), 7.55 (q, 1H, An-H), 7.41 (t, 1H, Ar-H), 7.32 (d, 2H, Ar-H), 6.68 (d, 1H, An-H), 3.01 (sept, 2H, CH(CH_3)), 1.22 (d, 6H, CH(CH_3)), 0.75 (d, 6H, CH(CH_3)) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ 189.8 (C=O), 162.3 (C=N), 146.9 (Ar-C), 138.4 (Ar-C), 138.2 (Ar-C), 135.1 (Ar-C), 132.1 (Ar-C), 129.9 (Ar-C), 128.8 (Ar-C), 128.0 (Ar-C), 127.8 (Ar-C), 126.2 (Ar-C), 125.7 (Ar-C), 125.4 (Ar-C), 124.1 (Ar-C), 122.6 (Ar-C), 27.9 (C-H), 23.9 (CH_3), 23.7 (CH_3) ppm. Elemental analysis: ($C_{25}H_{25}Br_2Cl_2NO$ Zn) (**3b.**$2CH_2Cl_2$) Calc. C 46.08, H 3.87, N 2.15; found C 45.71, H 3.43, N 1.99.

2.7 *Single-crystal x-ray structure determinations*

Single crystals of compound **1a**, **1b**, **1c**, **2b** and **3b** were grown from a solution of CH_2Cl_2 ($CHCl_3$ for **1a**) and pentane 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 Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic CuKα (1.54184 Å) and MoKα (0.71073 Å, for **2b**) radiation. Crystal data and structure refinement parameters are summarized in the table 1. The structures were solved by direct methods (SIR92)[24] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97.[25] Non-hydrogen atoms were anisotropically refined.

Table 1. Crystallographic structure refinement parameters of compound **1a-c**, **2b** and **3b**.

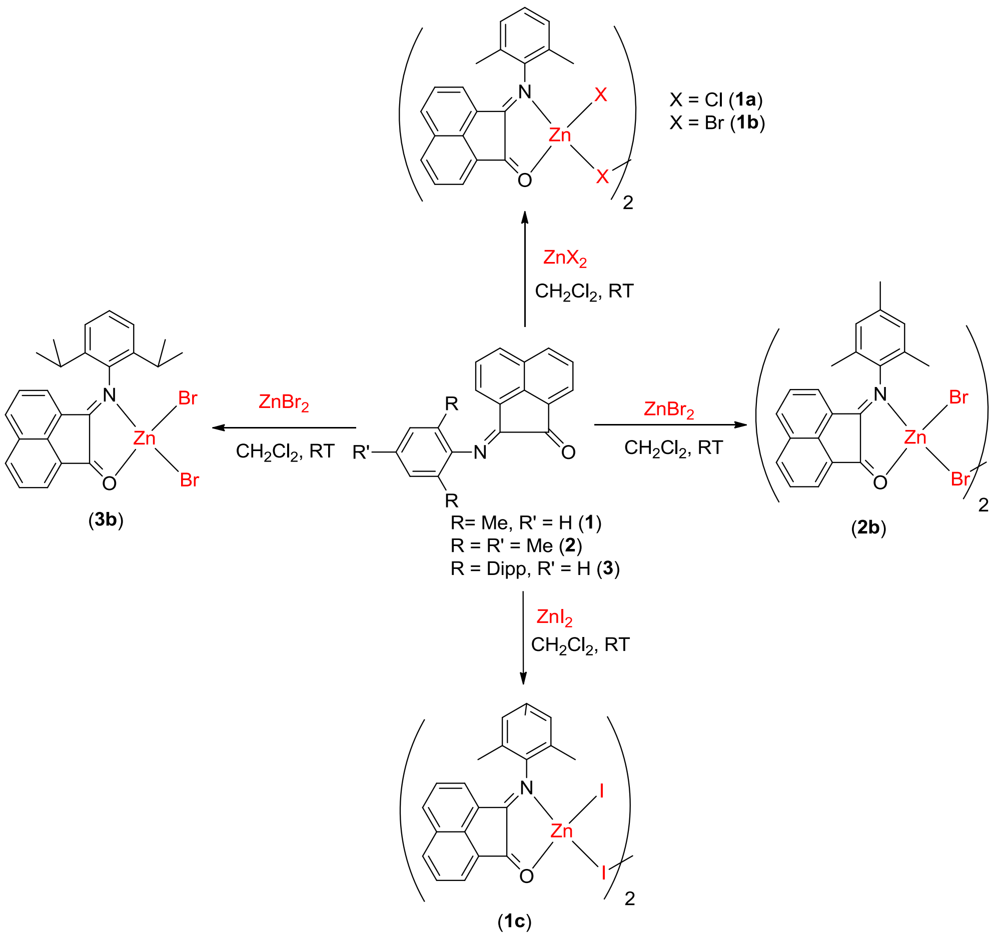
Compound	(**1a.** $\mathbf{CHCl_3}$)	(**1b.** $\mathbf{2CH_2Cl_2}$)	(**1c.** $\mathbf{CH_2Cl_2}$)	(**2b.** $\mathbf{2CH_2Cl_2}$)	(**3b.** $\mathbf{2CH_2Cl_2}$)
CCDC NO.	1003687	1003688	1003689	1003690	1003691
Empirical formula	$C_{42}H_{32}Cl_{10}N_2O_2$ Zn_2	$C_{44}H_{40}Br_4Cl_8N_2$ O_2Zn_2	$C_{42}H_{34}Cl_4I_4N_2O_2$ Zn_2	$C_{46}H_{42}Br_4Cl_8N_2O_2Zn_2$	$C_{25}H_{25}Br_2Cl_2NO$ Zn
Formula weight	1081.98	1362.76	1378.85	1388.80	651.55
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
space group	$C2/c$	P-1	P -1	P-1	$P\ 2_1/c$
a, [Å]	21.582(4)	10.0011(7)	9.9975(7)	10.6008(5)	10.9846(2)
b[Å]	10.6678(12)	11.6551(8)	10.5491(7)	11.0655(6)	22.4432(6)
c[Å]	23.718(3)	11.6837(10)	11.4155(8)	11.8075(6)	21.2265(3)
Alpha[^{o}]	90	105.093(6)	95.125(5)	103.848(4)	90
Beta[^{o}]	122.12(2)	102.068(6)	105.503(6)	101.399(4)	92.4480(10)
Gamma[^{o}]	90	96.284(5)	90.461(5)	93.204(4)	90
Volume, [Å^3]	4625.1(12)	1266.34(16)	1154.85(14)	1310.50(12)	5228.18(18)
Z	4	1	1	1	8
Calculated density (mg/m^3)	1.554	1.787	1.983	1.760	1.656
Temperature, K	293(2)	150(2)	150(2)	150(2)	150(2)
Wavelength	1.54184	1.54184	1.54184	0.71073	1.54184
Absorption coefficient	6.895	9.053	24.686	4.411	6.903
θ range for data collection[^{o}]	4.40 to 70.70	3.99 to 70.78	4.04 to 70.81	1.82 to 25.76	3.94 to 70.67
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Reflections collected	9519	8946	7606	8982	22231
Reflections Unique	4339 [R(int) = 0.0345]	4777 [R(int) = 0.0339]	4315 [R(int) = 0.0565]	4913 [R(int) = 0.0300]	9874 [R(int) = 0.0333]
Completeness to θ	97.5%	98.0%	97.2%	97.7%	98.3%
Data / restraints / parameters	4339 / 0 / 265	4777 / 0 / 281	4315 / 0 / 255	4913 / 0 / 292	9874 / 0 / 585
R indices (R_1; wR_2)	R1 = 0.0811; wR2 = 0.1923	R1 = 0.0503; wR2 = 0.1246	R1 = 0.0858; wR2 = 0.2262	R1 = 0.0542; wR2 = 0.1407	R1 = 0.0481; wR2 = 0.0862
GOOF	1.032	1.040	1.078	0.956	1.020

H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where P = (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.

3. Results and Discussion

The 2, 6-dimethylphenyl-BIAO ligand (**1**) was treated with anhydrous zinc dichloride in dichloromethane in a 1:1 molar ratio to afford [$ZnCl_2$(2,6-dimethylphenyl-BIAO)]$_2$ (**1a**) as orange solid in good yield (scheme 2). Other zinc complexes **1b**, **1c**, **2b** and **3b** were also isolated in similar reactions with respective Ar-BIAO ligands and zinc halides (scheme 2). The zinc complexes are soluble in THF, toluene, benzene and dichloromethane at room temperature. All the complexes were characterized by spectroscopic and analytical techniques. The solid state structures of all the complexes **1a–c**, **2b** and **3b** were characterized by single crystal X-ray diffraction analysis.

In FT-IR spectra, all the compounds **1a–c**, **2b** and **3b** show strong absorption bands at 1725, 1726, 1705, 1729 and 1726 cm^{-1} respectively for respective C=O bond stretching, which is slightly deviated from the C=O bond stretching frequencies of the corresponding ligands.[18,23] The strong absorption bands at 1645 (**1a**), 1650 (**1b**), 1645 (**1c**), 1648 (**2b**) and 1649 (**3b**) cm^{-1} can be assigned to C=N bond stretching of the iminoacenapthenone moiety. In the ^{1}H NMR spectrum measured in $CDCl_3$, compound **1a** shows a sharp singlet signal at 2.21 ppm which can be assigned to six protons from two methyl group at *o*-position of the phenyl group. For zinc dibromo and diiodo complexes **1b** and **1c**, the respective methyl protons appeared as sharp singlet at 2.29 and 2.36 ppm which is slightly low field shifted compared to that of **1a**. However, the chemical shift values are in similar ranges and the slight differences can be accounted for by the gradual increase in sizes from chlorine to iodine atom attached to the zinc atom.



Scheme 2. Synthesis of zinc complexes of **1a–c**, **2b** and **3b**.

However, these chemical shift values are slightly high field shifted with respect to the corresponding values of ligand **1** (δ 2.04 ppm). The multiplets in the range of 6.68–8.48 ppm for the complexes **1a**–**c** are due to the aromatic protons present in the phenyl group as well in the acenapthene moiety. Compound **2b** which has mesityl-BIAO ligand, shows two sharp singlets at 2.34 and 2.25 ppm in a 1:1 ratio and can be assigned to each of three methyl protons at *o*-positions of the phenyl group indicating the free rotation around the N(imine)-C(mesityl) is restricted in NMR time scale. The singlet resonance signal at 2.40 ppm for compound **2b** is assigned to the three methyl protons of the mesityl group at *p*-position. These chemical shifts are in the similar range with that of free ligand **2** (δ 2.04, six *o*-protons) and 2.35 (three *p*-protons)[23]. The resonances of the aryl protons present in acenaphthene back bone and aryl ring are in the expected region in between 6.91–8.46 ppm similar with the corresponding values of complexes **1a–c** and in well agreement with the free ligand **2**. For compound **3b**, where more bulky 2,6-disopropyl-BIAO ligand is present, two doublet signals at 0.74 and 1.22 ppm in 1:1 ratio and the coupling constants of (12 Hz) can be assigned to the methyl protons attached to the isopropyl groups and this is in similar range with that of free ligand **3** (δ 0.8 and 1.1 ppm).[18] The characteristic septet at 3.01 ppm corresponds to the resonance of the CH proton present in the isopropyl group is also observed slightly down field shifted than the corresponding value (2.80 ppm) of ligand **3**. The resonances of the protons of acenaphthene back bone and aryl ring for compound **3b** are also in the expected region between 6.68-8.40 ppm and in good agreement with the free ligand **3**. In ^{13}C {^{1}H} NMR spectra of the compounds **1a**–**c**, **2b** and **3b**, carbonyl carbon is mostly de-shielded and appear at δ = 189.3, 190.7, 189.7, 189.7 and 189.8 ppm respectively. The imine carbon is observed at 161.2, 162.7, 161.7, 164.3 and 162.3 ppm respectively and the *ipso* carbon attached to nitrogen atom is observed at 147.4, 147.8, 147.1, 147.0 and 146.9 ppm respectively for complex **1a–c**, **2b** and **3b**. These values are slightly shifted to the high field region compared to the respective Ar-BIAO ligands[18,23] due to the attachment of zinc ion.

3.1 *Solid state structures*

The compounds **1a**–**c**, **2b** and **3b** were re-crystallized from dichloromethane ($CHCl_3$ for **1a**) and pentane (1:1) mixture and their molecular structures in the solid state were established by single crystal X-ray diffraction analysis. Compound **1a** crystallizes in monoclinic space group $C2/c$ with four molecules in unit cell along with one chloroform molecule as solvate. In contrast, complexes **1b**, **1c** and **2b** crystallize in triclinic space group $P-1$ having only one molecule in their respective unit cell along with dichloromethane molecule (two for **1b** and **2b** and one for **1c**) as solvents. The details of structural and refinement parameters of all the complexes **1a**–**c** and **2b** are given in table 1. The molecular structures of complexes **1a**–**c** and **2b** are shown in figure 1a–d respectively.

The complexes **1a**–**c** and **2b** are dimeric in nature and two zinc ions are bridged through two μ_2-halide ions in each case. In complexes **1a**–**c**, the coordination polyhedron in each case is formed by the chelation of imine nitrogen, carbonyl oxygen atoms of the 2,6-dimethyl-BIAO ligand and the halide atoms (three chloride for **1a**, three bromide for **1b** and three iodide ions for **1c**) attached to the zinc ion. In similar fashion, the coordination polyhedron of compound **2b** is formed by the ligation of nitrogen and oxygen atoms present in mesityl-BIAO ligand and chloride ions. The complexes **1a**–**c** and **2b** are centrosymmetric due the presence of an inversion center in the middle of each of the molecule each of them form a four membered core Zn1-Cl1-Zn1^{i}-Cl1^{i} (**1a**), Zn1-Br1-Zn1^{i}-Br1^{i} (**1b** and **2b**), and Zn1-I1-Zn1^{i}-I1^{i} (**1c**). In addition, two more metallacycles are formed in each case Zn1-N1-C2-C1-O1 and Zn1^{i}-N1^{i}-C2^{i}-C1^{i}-O1^{i} (**1a**), Zn1-N1-C1-C2-O1 and Zn1^{i}-N1^{i}-C1^{i}-C2^{i}-O1^{i} (**1b**), Zn1-N1-C9-C10-O1 and Zn1^{i}-N1^{i}-C9^{i}-C10^{i}-O1^{i} (**1c**) and Zn1-N1-C1-C2-O1 and Zn1^{i}-N1^{i}-C1^{i}-C2^{i}-O1^{i} (**2b**). In these complexes, the geometry around each zinc ion can be best described either a distorted square pyramidal having N1, O1, Cl1, Cl1^{i} atoms for **1a**, N1, O1, Br2, Br2^{i} for **1b** and **2b**, N1, O1, I1, I1^{i} for **1c** in the basal position and Cl2 (**1a**), Br1 (**1b** and **2b**) and I1 (**1c**) atoms in the apical position or distorted trigonal bipyramidal having N1 Cl1 Cl2 atoms (for **1a**), N1 Br1 Br2 (for **1b** and **2b**) and N1 I1 I2 (for **1c**) are in the equatorial position and O1, Cl1^{i} (**1a**), O1, Br2^{i} (**1b** and **2b**), O1, I1^{i} (1c), atoms are in the apical position. Thus, all three complexes **1a**–**c** and **2b** are examples of unusual penta- coordinated zinc atom. Such kind of unusual zinc complexes are rare in literature.[26,27] The Zn-O distances [2.469(2) Å (**1a**), 2.484(3) Å (**1b**), 2.392(8) Å (**1c**) and 2.414(3) Å (**2b**)] which are well in agreement with the zinc oxygen coordination bond rather covalent bond (Zn-O 1.976 (2) Å for covalent bond.[27] The Zn1-N1 distances 2.087(3) Å (for **1a**), 2.073(3) Å (for **1b**), 2.104(8) Å (for **1c** and **2b**) 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 = $Me_2pzCH_2)_2NC_2H_3MeNHC_5H_6CSSCH_3$)

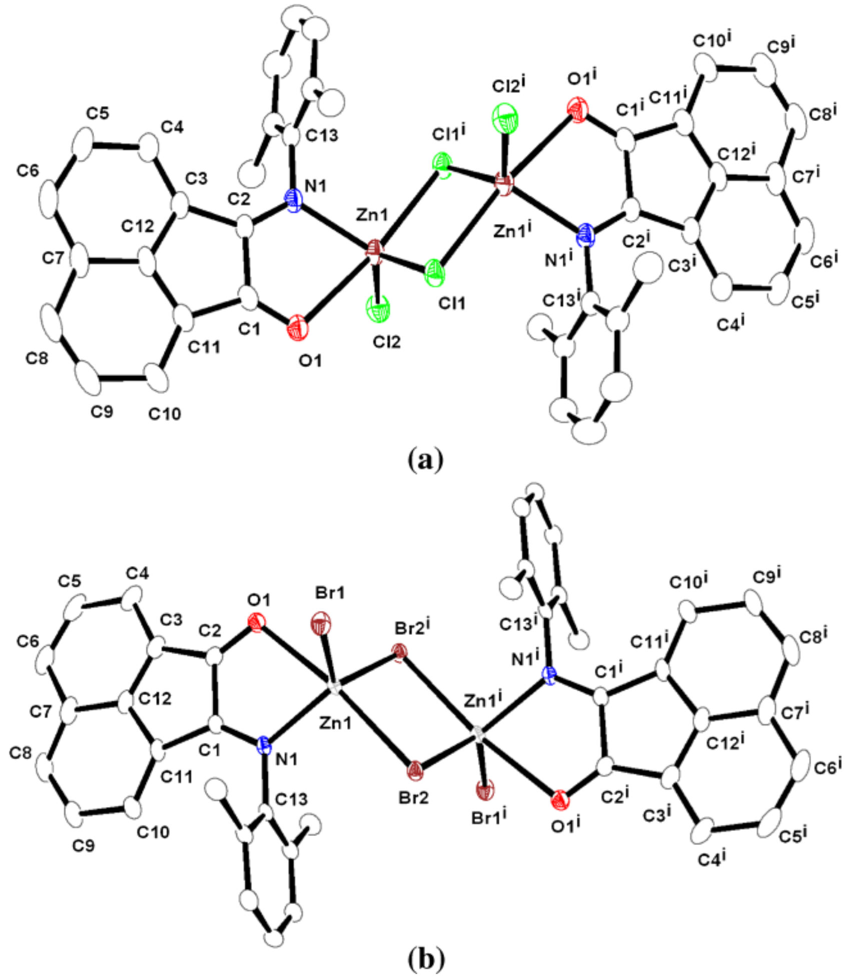


Figure 1. **a–d** Solid-state structures of **1a–c** and **2a** showing the atom labelling scheme omitting hydrogen atoms for clarity. Selected bond lengths in [Å]: **1a**. Zn(1)-N(1) 2.087(3), Zn(1)-Cl(2) 2.2103(15), Zn(1)-Cl(1) 2.3091(14), Zn(1)-Cl(1)^{i} 2.4404(13), Zn(1)-O(1) 2.468(3), Cl(1)-Zn(1)^{i} 2.4404(13), O(1)-C(1) 1.225(5), N(1)-C(2) 1.277(5), N(1)-C(13) 1.459(5), C(2)-C(3) 1.462(5), C(2)-C(1) 1.522(6), C(1)-C(11) 1.469(6); Selected bond angles in [^{o}]: N(1)-Zn(1)-Cl(2) 116.30(12), N(1)-Zn(1)-Cl(1) 115.46(11), Cl(2)-Zn(1)-Cl(1) 124.18(5), N(1)-Zn(1)-Cl(1)^{i} 96.67(10,) Cl(2)-Zn(1)-Cl(1)^{i} 104.78(5), Cl(1)-Zn(1)-Cl(1)^{i} 88.50(4), N(1)-Zn(1)-O(1) 74.84(12), Cl(2)-Zn(1)-O(1) 89.41(9), Cl(1)-Zn(1)-O(1) 84.97(9), Cl(1)^{i}-Zn(1)-O(1) 165.68(9,) Zn(1)-Cl(1)-Zn(1)^{i} 91.50(4), C(1)-O(1)-Zn(1) 105.5(3), C(2)-N(1)-C(13) 119.9(3), C(2)-N(1)-Zn(1) 118.9(3), C(13)-N(1)-Zn(1) 121.2(2), N(1)-C(2)-C(3) 134.5(4), N(1)-C(2)-C(1) 117.8(4), C(3)-C(2)-C(1) 107.7(4), O(1)-C(1)-C(11) 130.7(5), O(1)-C(1)-C(2) 122.7(4), C(11)-C(1)-C(2) 106.5(4), C(10)-C(11)-C(1) 132.9(5), C(12)-C(11)-C(1) 105.8(4). **1b.** Br(1)-Zn(1) 2.3266(6), Br(2)-Zn(1)^{i}1 2.4243(6), Br(2)-Zn(1) 2.5980(7), Zn(1)-N(1) 2.073(3), Zn(1)-Br(2)^{i}1 2.4243(6), Zn(1)-O(1) 2.483(3), O(1)-C(2) 1.223(5), N(1)-C(1) 1.274(5), N(1)-C(13) 1.455(5), C(1)-C(11) 1.464(5), C(1)-C(2) 1.536(5); Selected Bond Angles in [^{o}]: Zn(1)^{i}1-Br(2)-Zn(1) 88.50(2), N(1)-Zn(1)-Br(1) 116.29(9), N(1)-Zn(1)-Br(2)^{i}1 117.64(9), Br(1)-Zn(1)-Br(2)^{i}1 121.54(2), N(1)-Zn(1)-O(1) 74.91(11), Br(1)-Zn(1)-O(1) 89.52(7), Br(2)^{i}1-Zn(1)-O(1) 84.01(7), N(1)-Zn(1)-Br(2) 96.30(9), Br(1)-Zn(1)-Br(2) 103.50(2), Br(2)^{i}1-Zn(1)-Br(2) 91.50(2), O(1)-Zn(1)-Br(2) 166.65(7), C(2)-O(1)-Zn(1) 105.8(3), C(1)-N(1)-C(13) 118.8(3), C(1)-N(1)-Zn(1) 118.6(3), C(13)-N(1)-Zn(1) 122.4(2) N(1)-C(1)-C(11) 134.2(4), N(1)-C(1)-C(2) 119.0(3), C(11)-C(1)-C(2) 106.9(3), O(1)-C(2)-C(3) 132.7(4), O(1)-C(2)-C(1) 121.4(4).

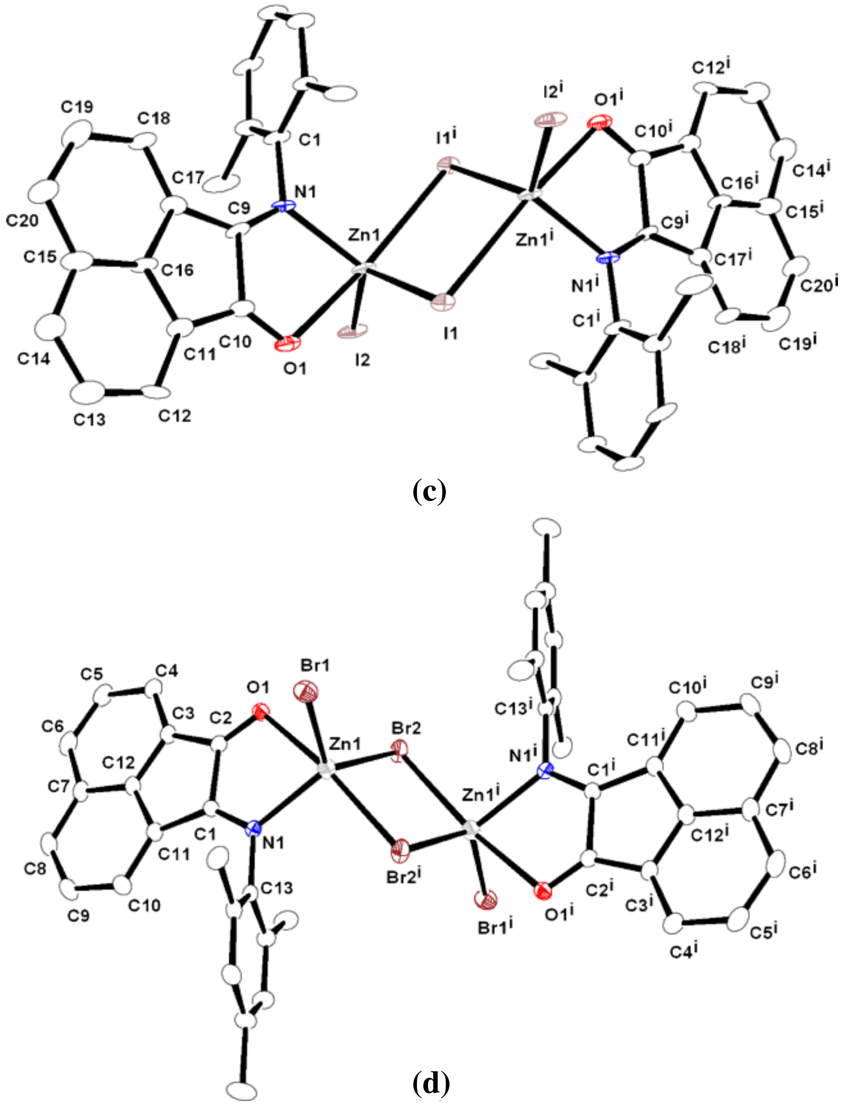


Figure 1. **1c.** I(1)-Zn(1) 2.6529(13), I(1)-Zn(1)^{i}1 2.8263(15), I(2)-Zn(1) 2.5377(13), Zn(1)-N(1) 2.104(8), Zn(1)-O(1) 2.392(8), Zn(1)-I(1)^{i}1 2.8263(15), O(1)-C(10) 1.222(14), N(1)-C(9) 1.259(13), N(1)-C(1) 1.452(11), C(2)-C(1) 1.409(14); Selected Bond Angles in [°]: Zn(1)-I(1)-Zn(1)^{i}1 87.89(4), N(1)-Zn(1)-O(1) 76.0(3), N(1)-Zn(1)-I(2) 118.0(2), O(1)-Zn(1)-I(2) 91.63(19), N(1)-Zn(1)-I(1) 111.4(2), O(1)-Zn(1)-I(1) 80.23(18), I(2)-Zn(1)-I(1) 126.07(5), N(1)-Zn(1)-I(1)^{i}1 95.6(2), O(1)-Zn(1)-I(1)^{i}1 165.42(19), I(2)-Zn(1)-I(1)^{i}1 102.89(5), I(1)-Zn(1)-I(1)^{i}1 92.11(4), C(10)-O(1)-Zn(1) 106.7(6), C(9)-N(1)-C(1) 119.0(8), C(9)-N(1)-Zn(1) 117.2(6), C(1)-N(1)-Zn(1) 123.8(6). **1d.** Br(2)-Zn(1) 2.4512(7), Br(2)-Zn(1)^{i}1 2.5639(7), Br(1)-Zn(1) 2.3435(7), Zn(1)-N(1) 2.104(4), Zn(1)-O(1) 2.414(3), Zn(1)-Br(2)^{i}1 2.5639(7), O(1)-C(2) 1.212(6), N(1)-C(1) 1.286(6), N(1)-C(13) 1.442(5), C(1)-C(11) 1.466(6), C(1)-C(2) 1.535(6), C(2)-C(3) 1.466(6); Selected bond Angles in [°]: Zn(1)-Br(2)-Zn(1)^{i}1 89.08(2), N(1)-Zn(1)-Br(1) 114.62(10), N(1)-Zn(1)-O(1) 75.58(12), Br(1)-Zn(1)-O(1) 87.64(8), N(1)-Zn(1)-Br(2) 117.29(10), Br(1)-Zn(1)-Br(2) 122.18(3), O(1)-Zn(1)-Br(2) 82.14(8), N(1)-Zn(1)-Br(2)^{i}1 96.74(10), Br(1)-Zn(1)-Br(2)^{i}1 106.71(3), O(1)-Zn(1)-Br(2)^{i}1 165.60(8), Br(2)-Zn(1)-Br(2)^{i}1 90.92(2), C(2)-O(1)-Zn(1) 107.3(3), C(1)-N(1)-C(13) 118.9(4), C(1)-N(1)-Zn(1) 117.3(3), C(13)-N(1)-Zn(1) 123.7(3), N(1)-C(1)-C(2) 117.6(4), O(1)-C(2)-C(3) 131.4(4), O(1)-C(2)-C(1) 122.1(4), C(3)-C(2)-C(1) 106.5(4).

(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.*[29] Three different Zn-halide distances in each complex [Zn-Cl 2.210(2), 2.309(2), 2.440(1), Å for **1a**; Zn-Br 2.327(6), 2.424(6), 2.598(7) Å for **1b**; Zn-I 2.536(1), 2.653(1), 2.826(2) Å for **1c** and Zn-Br 2.343(7), 2.451(7), 2.564(7) Å for **2b**] indicate that one halide ion is purely covalent bonded, whereas second halide ion is bonded covalently as well as in bridging fashion which elongate Zn-halide distance slightly, and the third halide ion is purely a coordination bond and has the longest Zn-halide distance. Thus, an asymmetric attachment of the halide ions to the zinc centres are observed in each complexes. The average distance of 2.217(7) Å was observed as Zn-Cl distance in $BIANZnCl_2$[30] and 2.337–2.347 Å was reported as Zn-Br distance (ZrBr2(TEEDA)) (tetraethylethylenediamine) in literature.[31] The Zn-I bond distance of 2.550(8)–2.553(7) Å is reported for $BIANZnI_2$ by Schumann *et al.*[30]

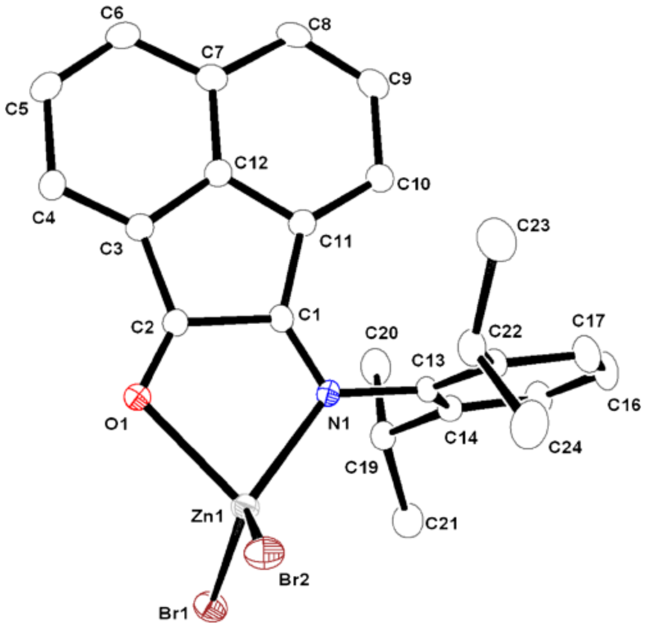


Figure 2. Solid-state structure of **3b** showing the atom labelling scheme omitting hydrogen atoms for clarity. Selected bond lengths in [Å]: Zn(1)-N(1) 2.086(2), Zn(1)-O(1) 2.162(2), Zn(1)-Br(1) 2.3181(6), Zn(1)-Br(2) 2.3280(6), O(1)-C(2) 1.227(4), N(1)-C(1) 1.278(4), N(1)-C(13) 1.460(4), C(1)-C(11) 1.460(4), C(1)-C(2) 1.539(4), C(2)-C(3) 1.463(4); Selected bond angles in [°]: N(1)-Zn(1)-O(1) 81.03(9), N(1)-Zn(1)-Br(1) 114.77(7), O(1)-Zn(1)-Br(1) 107.52(6), N(1)-Zn(1)-Br(2) 113.13(7), O(1)-Zn(1)-Br(2) 104.90(6), Br(1)-Zn(1)-Br(2) 125.08(2), C(2)-O(1)-Zn(1) 109.00(19), C(1)-N(1)-C(13) 118.1(3), C(1)-N(1)-Zn(1) 111.5(2), C(13)-N(1)-Zn(1) 130.30(19), N(1)-C(1)-C(11) 135.3(3), N(1)-C(1)-C(2) 117.4(3), O(1)-C(2)-C(3) 132.4(3), O(1)-C(2)-C(1) 121.0(3), C(3)-C(2)-C(1) 106.5(3).

The monomeric zinc complex **3b** crystallizes in monoclinic space group $P2_1/c$ having two independent molecules in the unit cell along with two dichloromethane molecules. The details of structural and refinement parameters of the complex **3b** are given in table 1. The molecular structure of complex **3b** is shown in figure 2. The central ion zinc is tetracoordinated through nitrogen and oxygen atoms present in the 2,6-diisopropylphenyl-BIAO ligand and two bromide ions attached to zinc. The geometry around the zinc can be best described as distorted tetrahedral. With respect to the dimeric complexes **1a–c** and **2b**, the monomeric form of **3b** can be understood due to the presence of 2,6-isopropylphenyl group on the iminoacenapthenone moiety which prevents the formation of dimer. The Zn-O distances [2.162(2) and 2.154(2) Å

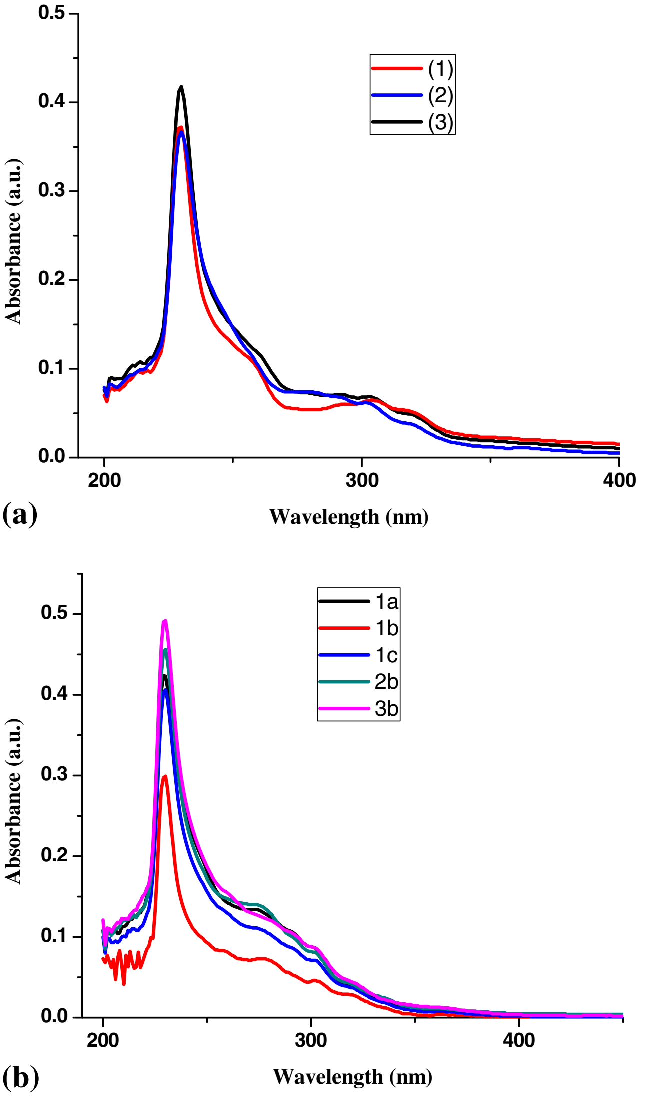


Figure 3. a-b. The UV-vis absorption spectra of ligands **1–3** and zinc complexes **1a–c**, **2b** and **3b** in CH_2Cl_2 at room temperature (3.207×10^{-6} M) respectively.

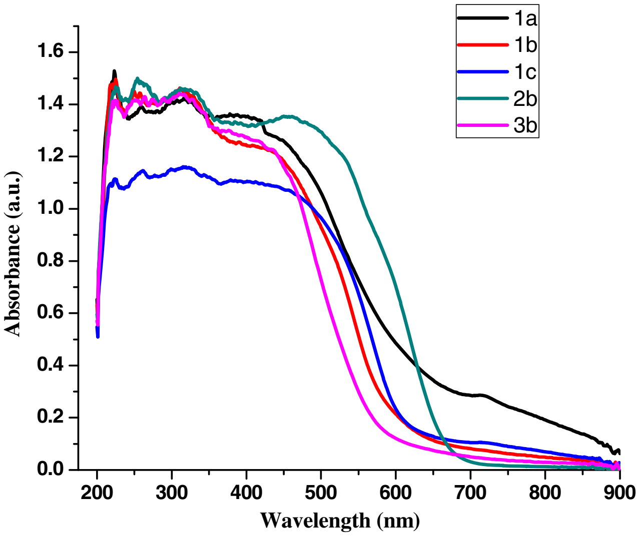


Figure 4. The solid state UV-vis absorption spectra of complexes **1a–c**, **2b** and **3b**.

for molecule 1 and 2 respectively] are slightly shorter than that of complexes **1a–c** and **2b** (see above). This can be explained due to expansion of coordination number from four to five for zinc ion as we move from tetrahedral geometry of **3b** to trigonal bipyramidal geometry of **1a–c** and **2b**. Nevertheless, the Zn-N distances [2.086(2) and 2.105(2) Å for molecule 1 and 2 respectively] are in the similar range with that of **1a–c** and **2b**. The Zn-Br distances [2.318(6) and 2.328(6) Å for molecule 1 and 2.307(6) and 2.332 (6) Å for molecule 2) are also similar with that of zinc complexes **1b** and **2b**. In **3b**, the four membered zinc metallacycles Zn1-N1-C1-C2-O1 (molecule 1) and Zn2-N2-C25-C26-O1 (molecule 2) are formed and almost co-planar with the acenapthene plane (dihedral angle 6.79°).

3.2 *UV-visible spectra*

UV-visible absorption spectra of Ar-BIAO ligands **1**, **2** and **3** (figure 3a) were measured in dichloromethane at room temperature and displayed a nearly comparable absorption pattern at 230, 303 nm. The absorption spectra of the ligands **1**, **2** and **3** can be attributed to the $\pi \rightarrow \pi^*$ transitions and n $\rightarrow \pi^*$ transitions respectively. The UV-visible absorption spectra of complexes **1a**, **1b**, **1c**, **2b** and **3b** (figure 3b) were also measured in dichloromethane at room temperature and displayed a similar kind of absorption pattern at 230 nm for $\pi \rightarrow \pi^*$ transition. Upon coordination with zinc (II) ion, the absorption peaks are slightly shifted compared to that of the respective ligands. The solid-state UV-visible absorption spectra of **1a**, **1b**, **1c**, **2b**, **3b** were significantly different from that of solution (figure 4). In the solid-state UV-visible absorption spectra of **1a**, **1b**, **1c**, **2b**, **3b** a broad absorption peak from 250 to 500 nm were attributed to the π to π^* transition of ligand. In the solid-state UV-visible absorption spectra of all zinc (II) complexes, the $\pi \rightarrow \pi^*$ transition intensity is in the same order for complexes **1a**, **1b**, **2b** and **3b** but for complex **1c,** the intensity drastically decreases compared to that of other complexes.

4. Conclusion

We have successfully synthesized and characterized four dimeric penta-coordinated zinc complexes $[ZnCl_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**1a**), $[ZnBr_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**1b**), $[ZnI_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**1c**) and $[ZnBr_2(\text{Mes-BIAO})]_2$ (**2b**) along with one tetra-coordinated monomeric zinc complex $[ZnBr_2(\text{Dipp-BIAO})]$ (**3b**). The molecular structures of all the complexes were established and they revealed a bidentate ligation from the Ar-BIAO ligands in each case through lone pairs of nitrogen and oxygen atoms. Thus, it was observed that by changing the steric crowding on the Ar-BIAO ligand, the nuclearity of the zinc complexes can be changed.

Supplementary Information

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 1003687-1003691. 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).

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