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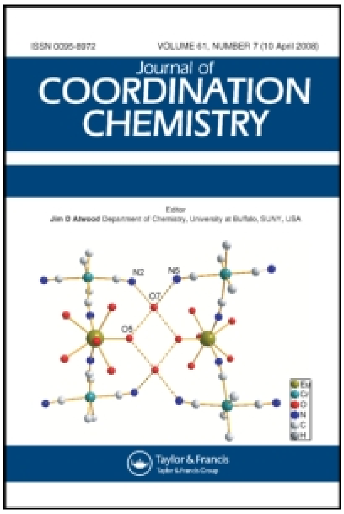

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The Crystal Structure of Bis[*N*-(2,6-diisopropylphenyl)imino] Acenaphthene and Studies of its Copper(I) and Copper(II) Complexes

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THE CRYSTAL STRUCTURE OF BIS[*N*-(2,6-DIISOPROPYLPHENYL)IMINO] ACENAPHTHENE AND STUDIES OF ITS COPPER(I) AND COPPER(II) COMPLEXES

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The crystal structure of the rigid bidentate nitrogen ligand bis[*N*-(2,6-diisopropylphenyl)imino]acenaphtene (o,o'-iPr$_2$C$_6$H$_3$-BIAN) is described. Syntheses, electronic spectra and electrochemical properties of two copper complexes containing (o,o'-iPr$_2$C$_6$H$_3$–BIAN), namely, [CuCl(o,o'-iPr$_2$C$_6$H$_3$–BIAN)$_2$]Cl (**1**) and [Cu(o,o'-iPr$_2$C$_6$H$_3$-BIAN)$_2$](ClO$_4$)(AcOH)$_2$ (**2**), where AcOH = acetic acid, are reported. Although in both complexes two o,o'-iPr$_2$C$_6$H$_3$-BIAN ligands are coordinated, geometries about the copper atom are significantly different. While complex **2** displays a strongly "flattened" distortion towards square-planar geometry, in complex **1** square-pyramidal coordination with an almost perfect planar arrangement of two o,o'-iPr$_2$C$_6$H$_3$–BIAN ligands around the copper centre is suggested.

Keywords: Copper; N ligands; X-ray structure determination; Electronic spectroscopy

INTRODUCTION

Rigid bidentate ligands such as bis(*N*-arylimino)acenaphthene, Ar-BIAN, and their complexation with late transition metals has increased use in catalysis [1–5]. These Ar-BIAN ligands contain two conjugated imine functions, but are markedly different from other diimine ligands such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). First, the presence of two exocyclic imines which are not part of a heteroaromatic ring system is expected to lead to better σ-donating and better π-accepting properties as compared to phen and bpy [6,7]. Secondly, the rigid acenaphthene backbone prevents rotation around the imine carbon–carbon bond and forces the imine N atoms to remain in a fixed *cis* orientation, favouring chelating coordination to a metal centre [8].

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Copper complexes containing chelating diimine ligands are finding increasing use as catalysts for a wide range of synthetic organic reactions [9–11] and as suitable systems for molecular solar-energy conversion and molecular sensing [12–15]. Another interesting quality inherent in copper coordination compounds with diimines is the structural difference between the Cu(I) and Cu(II) oxidation state [16]. Although copper(I) prefers to be four-coordinate with nearly tetrahedral geometry, crystal structure studies of many $\mathrm{Cu^1(NN)_2^+}$ systems show considerable deviation from the geometry [17–20]. Most commonly, the angle between the two diimine ligands is less than 90°. This flattening of the ligands (towards square-planar geometry) lowers the symmetry from D_{2d} to D_2 (Fig. 1) [21].

In this work we report the crystal structure of the *o*,*o*′-$i\mathrm{Pr_2C_6H_3}$-BIAN ligand including a comparison with other similar compounds. In addition, we focus on a comparative study, including electronic, electrochemical and structural properties, of two copper(II) and copper(I) complexes, namely, [CuCl(*o*,*o*′-$i\mathrm{Pr_2C_6H_3}$-BIAN)$_2$]Cl (**1**) and [Cu(*o*,*o*′-$i\mathrm{Pr_2C_6H_3}$-BIAN)$_2$](ClO$_4$)(AcOH)$_2$ (**2**). Interestingly, the (*o*,*o*′-$i\mathrm{Pr_2C_6H_3}$-BIAN) ligand with two conjugated imine *N*-atoms that are not part of the heteroaromatic ring system leads to the stabilization of both the higher and lower oxidation states of the coordinated metal ions [22].

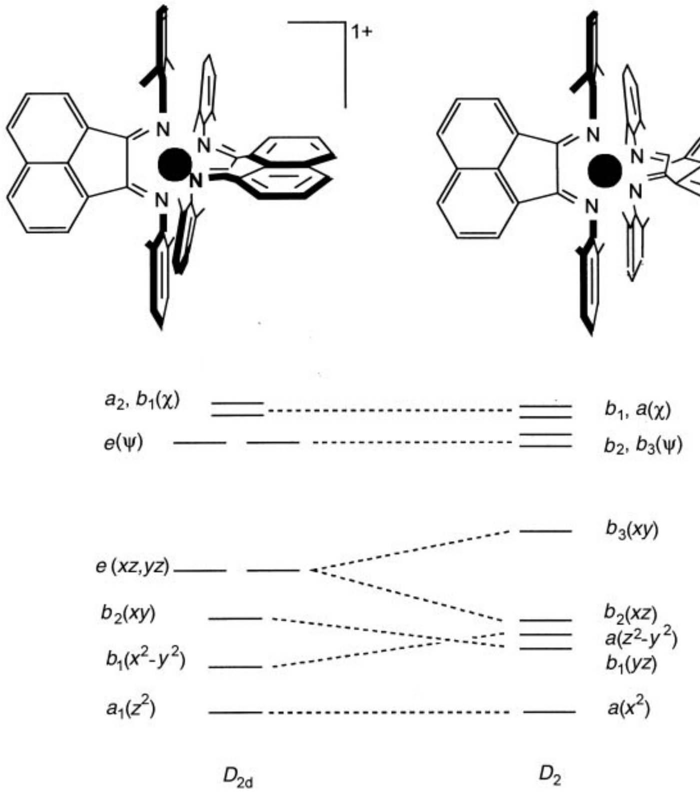

FIGURE 1 Schematic orbital splitting diagram for [Cu(*o*,*o*′-$i\mathrm{Pr_2C_6H_3}$-BIAN)$_2$]$^+$ (**2**), showing the flattening towards square-planar geometry as a result of lowering of the symmetry from D_{2d} to D_2. The flattening distortion is assumed to occur along the x axis.

EXPERIMENTAL

Materials and Instrumentation

All starting materials were purchased from Wako Pure Chemical Industries Ltd., and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 Series II CHNSIO instrument. Electronic spectra were recorded on a UV-3100PC Shimadzu spectrophotometer using 10 mm quartz cells at room temperature. Powder reflectance spectra were obtained using the same instrumental equipped with an integrating sphere and using $BaSO_4$ as reference. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer using KBr pellets and Nujol mulls in the 4000–370 cm^{-1} range. ^1H and ^{13}C NMR measurements at room temperature were run on a JEOL JNM LA 300 WB spectrometer at 300.40 and 75.45 MHz, respectively, using a 5 mm probe head with CD_2Cl_2 with $CDCl_3$ solvents. Chemical shifts are given in ppm relative to internal TMS. A typical pulse width was 6.25 μs for ^1H and 4.25 μs for ^{13}C NMR measurements. Thermogravimetric measurements were performed on a Shimadzu DTG-50 instrument.

[N-(2,6-diisopropylphenyl)imino]acenaphthene

The o,o'-$i$$Pr_2C_6H_3$-BIAN ligand was synthesized from acenaphthenequinone and 2,6-diisopropylaniline as follow: 1.35 g (7.4 mmol) of acenaphthenequinone in 65 ml of acetonitrile was refluxed (80°C) for 30 min, then 12 ml of acetic acid was added and heating was continued until the acenaphthenequinone had completely dissolved. To this hot solution, 3 ml (16 mmol) of 2,6-diisopropylaniline was added directly and the solution was heated under reflux for further 1.5 h. It was then cooled to room temperature and the solid filtered off to give a yellow product that was washed with hexane and air-dried. Crystals suitable for X-ray measurements were obtained by recrystallization from hot hexane. Yield: 3.15 g (85%). Found (%): C, 85.85; H, 8.03; N, 5.3. Calc. for $C_{36}H_{40}N_2$: C, 86.35; H, 8.05; N, 5.60. ^1H NMR ($CDCl_3$, 24°C) $\delta = 0.97$ (d, H23), 1.23 (d, H24), 3.03 (sept, H22), 6.63 (d, H2), 7.26 (s, H15, H16, H17), 7.36 (pst, H3), 7.88 (d, H4). ^{13}C NMR (CD_2Cl_2, 24°C): $\delta = 23.1$ (C23), 23.3 (C24), 29.1 (C22), 123.5 (C16), 123.9 (C15, C17), 124.6 (C2), 128.3 (C3), 129.2 (C4), 130.0 (C1), 131.6 (C5), 135.5 (C14, C18), 141.2 (C10), 148.0 (C13), 161.1(C11).

[CuCl(o,o'-$i$$Pr_2C_6H_3$-BIAN)$_2$]Cl (1)

Some 0.1 g (7.4×10^{-4} mol) of $CuCl_2$ and 0.74 g of o,o'-$i$$Pr_2C_6H_3$-BIAN ($1.48 \times 10^{-3}$ mol) where mixed and 25 ml of acetic acid was added. After 2 h stirring at room temperature, the dark-green product was filtered off, washed with dichloromethane and dried *in vacuo*, yielding 42% of **1**. Found (%): C, 76.05; H, 6.86; N, 4.7 Calc. for $C_{72}H_{80}Cl_2N_4Cu$: C, 76.13; H, 7.10; N, 4.93; $\mu_{eff} = 1.76$ B.M. (24°C).

[Cu(o,o'-$i$$Pr_2C_6H_3$-BIAN)$_2$]($ClO_4$)(AcOH)$_2$ (2)

Some 0.13 g (3.51×10^{-4} mol) of $Cu(ClO_4)_2.6H_2O$ and 0.35 g (7.02×10^{-4} mol) of o,o'-$i$$Pr_2C_6H_3$-BIAN were mixed in 40 ml of acetic acid and heated to reflux. After 6 h the mixture was cooled to room temperature and the solid filtered off.

The red-brown product was washed with dichloromethane and dried in vacuum. Yield: 58% of **2**. Found (%): C, 71.04; H, 6.86; N, 4.59. Calc. for $C_{76}H_{88}ClN_4O_8Cu$: C, 71.06; H, 6.91; N, 4.36; μ_{eff} (24°C): diamagnetic ^{1}H NMR (CD_2Cl_2, 24°C): $\delta = 1.05$ (d, H23), 1.27 (d, H24), 2.97 (sept, H22), 6.97 (d, H4), 7.43 (s, H15, H16, H17), 7.45 (s, H27, H28, H29), 7.52 (pst, H3), 7.64 (pst, H7), 8.30 (d, H4). ^{13}C NMR (CD_2Cl_2, 24°C): $\delta = 23.5$ (C23), 23.1 (C24), 29.7 (C22), 125.1 (C15, C17), 125.5 (C2), 129.2 (C3), 129.9 (C4), 131.6 (C5), 139.2 (C14, C18), 144.9 (C10), 163.2 (C11).

X-ray Data Collection and Structure Refinement

Crystallographic data, conditions used for the data collection and refinement for *o*,*o*′-*i*$Pr_2C_6H_3$-BIAN are summarized in Table I. A prismatic crystal ($0.5 \times 0.3 \times 0.1\,mm^3$) was mounted on a Rigaku AFC7R diffractometer using graphite-monochromated CuKα radiation at 293 K. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 20 reflections in the range $4.07 < \theta < 67.97°$. The $\omega - 2\theta$ scan mode with a maximum 2θ value being 136° was used to collect intensity data. A total of 3363 reflections were collected, of

TABLE I Crystallographic data and structure refinement details for *o*,*o*′-*i*$Pr_2C_6H_3$-BIAN

Crystal data	
Empirical formula	$C_{36}H_{40}N_2$
Formula weight	500.7
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	15.587(2)
b (Å)	8.856(2)
c (Å)	21.780(7)
α, γ (°)	90.00
β (°)	93.85(2)
V (Å^3)	2999.8(12)
Z	4
Crystal dimensions (mm)	$0.5 \times 0.3 \times 0.1$
D_{calcd} (g cm^{-3})	1.109
F(000)	1080
μ (mm^{-1})	0.481
Data collection	
Temperature (K)	293(2)
θ range (°)	4.07–67.97
Radiation	Cu$K\alpha$, 1.54178 Å
Scan mode	$\omega - 2\theta$
Index ranges	$-18 \leq h \leq 12$; $0 \leq k \leq 10$; $-26 \leq l \leq 26$
Reflections collected	3363
Independent reflections	3363 (R(int) = 0.000)
Refinement	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3345/2/344
Goodness-of-fit on F^2	1.155
Final R indices ($I > 2.00\sigma(I)$)	$R_1 = 0.0495$, $wR_2 = 0.1550$
R indices (all data)	$R_1 = 0.0666$, $wR_2 = 0.1812$
Absolute structure parameter	−0.7 (9)
Extinction coefficient	0.00034 (14)
Largest diff. peak and hole	0.237and −0.188 eÅ^{-3}

which 3353 had $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-86 [23] and refined on F^2 using SHELXS-98 [24]. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were included, but their positions were not refined. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-183689. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Crystal Structure of o,o'-iPr$_2$C$_6$H$_3$-BIAN

An ORTEP plot with the atom numbering scheme of o,o'-iPr$_2$C$_6$H$_3$-BIAN is depicted in Fig. 2. Selected bond lengths, angles and torsion angles are compiled in Table II. The X-ray structure of o,o'-iPr$_2$C$_6$H$_3$-BIAN confirms a nearly perfect planar arrangement of the bis(imino)acenaphthene skeleton as evidenced by torsion angles N(1)–C(11)–C(12)–N(2), $-0.79(0.29)^\circ$ and C(1)–C(11)–C(12)–C(9), $-1.70(0.21)^\circ$. Comparison to the analogous species bis(p-tolylimino)acenaphthene (p-Tol-BIAN) shows a less planar arrangement of the latter with corresponding torsion angles of $-6.5(3)$ and $-5.6(2)^\circ$, respectively [6]. A more planar arrangements of the free (o,o'-iPr$_2$C$_6$H$_3$-BIAN) ligand is reported upon coordination to a metal centre, as in case of the copper(II) complex, namely, [Cu(AcOH) (o,o'-iPr$_2$C$_6$H$_3$-BIAN)Cl$_2$]

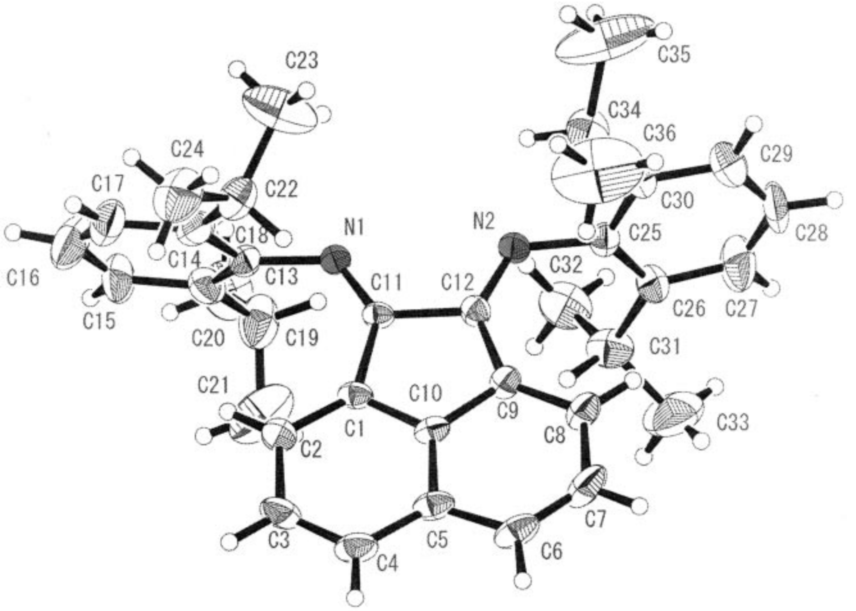

FIGURE 2 An ORTEP plot of the o,o'-iPr$_2$C$_6$H$_3$-BIAN ligand.

TABLE II Selected bondlengths (Å), angles (°), and torsion angles (°) for (*o,o′*-*i*Pr$_2$C$_6$H$_3$-BIAN)

N(1)–C(11)	1.250(6)
N(1)–C(13)	1.418(6)
N(2)–C(12)	1.295(6)
N(2)–C(25)	1.421(5)
C(1)–C(2)	1.37(7)
C(1)–C(10)	1.402(7)
C(1)–C(11)	1.505(5)
C(2)–C(3)	1.422(8)
C(11)–C(12)	1.526(3)
C(13)–C(14)	1.417(8)
C(13)–C(18)	1.397(7)
C(14)–C(15)	1.393(8)
C(15)–C(16)	1.384(11)
C(16)–C(17)	1.346(12)
C(17)–C(18)	1.387(8)
C(11)–N(1)–C(13)	123.3(4)
C(12)–N(2)–C(25)	122.8(4)
C(2)–C(1)–C(10)	120.3(5)
N(1)–C(11)–C(1)	133.8(4)
N(1)–C(11)–C(12)	122.2(4)
C(1)–C(11)–C(12)	104.0(4)
N(1)–C(11)–C(12)–N(2)	− 0.79(0.29)
C(1)–C(11)–C(12)–C(9)	− 1.70(0.21)
C(11)–N(1)–C(13)–C(14)	− 104.46(0.6)
C(11)–N(1)–C(13)–C(18)	83.88(0.61)
C(12)–N(2)–C(25)–C(30)	− 105.25(0.64)
C(12)–N(2)–C(25)–C(26)	82.64(0.61)
C(1)–C(11)–C(12)–N(2)	179.40(0.48)
C(1)–C(11)–C(12)–C(9)	− 1.70(0.21)
N(1)–C(11)–C(12)–C(9)	178.15(0.51)
C(14)–C(13)–N(1)–C(11)	− 104.46(0.60)
C(18)–C(13)–N(1)–C(11)	83.88(0.61)

(where AcOH = acetic acid) with corresponding torsion angles of − 0.3(3) and − 0.4(3)°, respectively [25].

The imine C=N bond of 1.275(6) Å (mean value) is comparable to the exocyclic C=N bond in c-Hex-DAB [1.258(3) Å] (c-Hex-DAB = 1,4,dicyclohexyl-1,4-diaza-1,3-butadiene) [26] and is shorter than C–N bonds in 2,2′-bipyridine [1.34 Å] [27] and 2,2′-biquinoline [1.323(2) Å] [28], that are parts of a heteroaromatic ring system. The bond lengths N(1)–C(11), 1.250(6) Å, and C(1)–C(11), 1.505(6) Å, are near to standard N(sp^2) = C(sp^2) and C(sp^2) = C(sp^2) double bonds (1.27 and 1.48 Å, respectively) [29] which implies that the structure can be regarded as a diimine bridged by naphthalene to keep the imine groups in a fixed *cis* orientation and not a conjugated 14-electron π-system.

Aromatic N substituents make an angle of (76°) with the plane of the naphthalene backbone, larger than the corresponding angle (61°) in the case of (*p*-Tol-BIAN) [8]. Upon coordination to a metal centre, more perpendicular angles of (84 and 87°) are observed with the two copper(II) complexes [Cu(AcOH)(*o,o′*-*i*Pr$_2$C$_6$H$_3$-BIAN)Cl$_2$] and [Cu(acac)(AcOH)(*o,o′*-*i*Pr$_2$C$_6$H$_3$-BIAN)] · (ClO$_4$) (acac = acetylacetonate) [30]. In these complexes the diisopropylphenyl groups are bent toward the naphthalene backbone and away from the copper centre resulting in a nearly perpendicular angle between the planes comprising naphthalene and the aromatic N substituents.

Infrared Spectra

Infrared data for the free *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand and complexes **1** and **2** are listed in Table III. Bands assigned to ν(C=N) in the free ligand are observed at 1671, 1652 and 1642 cm^{-1}. These shift to lower wavenumbers in the spectra of complexes indicating the coordination of both diimine nitrogen atoms of *o,o′*-*i*$Pr_2C_6H_3$-BIAN to the copper centre in both complexes. In the complexes, the coordination of two *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligands is confirmed by the splitting of the out-of-plane CH deformation vibration bands in the 810–750 cm^{-1} region.

Electronic Spectra

Electronic data for complex **1** in various solvents and in the solid state are shown in Table IV. The *d–d* broad band at around 630 nm is typical of square-pyramidal copper(II) complexes [31]. This structure is stabilized by introducing a chloride atom to the $Cu^{II}(NN)_2$ coordination sphere. In absence of chloride, the central copper ion is readily reduced from Cu(II) to Cu(I). This behaviour is similar to that in the 2,9-dimethyl-1,10-phenanthroline-copper(II) system. For complex **2** (in absence of chloride coordination) a distorted tetrahedral geometry around Cu(I) is suggested.

Solid and in solution electronic spectra of **2** show a low-energy shoulder in the 565–580 nm range (Table V). This shoulder is assigned as a MLCT transition [$3d(Cu)\rightarrow\pi^*$ (diimine)] [21,32]. In D_{2d} symmetry the excited state corresponds to a $^1B_2$ term associated with an $e(xz,yz)\rightarrow e(\psi)$ excitation wherein the first approximation

TABLE III IR data (cm^{-1}) for *o,o′*-*i*$Pr_2C_6H_3$-BIAN and complexes **1** and **2**

Compound	$\nu(C=N)$	*CH deformation vibrations*
o,o′-*i*$Pr_2C_6H_3$-BIAN	1671, 1652, 1642	755, 787, 810
1	1661, 1635	753, 779, 788, 809
2	1669, 1633	757, 781, 784, 810

TABLE IV Electronic spectroscopic data for **1** at room temperature[a]

	λ_{max} (nm)		
Solid	632	421	
DCE	[b]	415(8000)[a]	367(7500)
Chloroform	[b]	415(7300)	379(6300)
Toluene	635(1320)	440(6580)	364(7200)
THF	[b]	433(8200)	365(7200)

[a]The ε values are given in parentheses; [b]not observed because of low solubility.

TABLE V Electronic spectroscopic data for **2** at room temperature[a]

	λ_{max} (nm)			
Solid	576(sh)	480	458	
DCE	564(sh)	494(6000)[a]	459(8000)	435(7000)
Chloroform	569(sh)	458(5500)	432(6300)	405(5600)
Toluene	580(sh)	455(1100)	425(1300)	
THF	569(sh)	460(4200)	435(4700)	

[a]The ε values are given in parentheses.

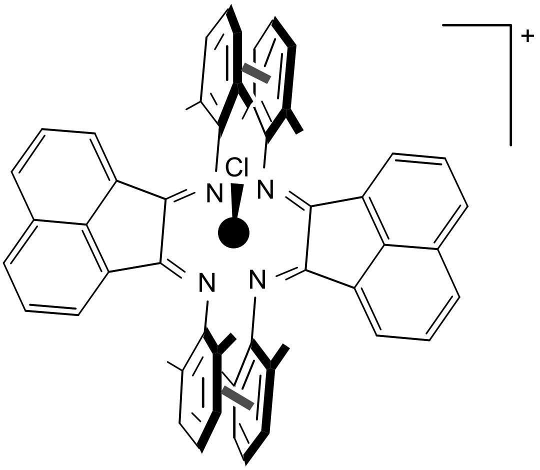

FIGURE 3 Proposed structure of [CuCl(o,o'-iPr$_2$C$_6$H$_3$-BIAN)$_2$]Cl (**1**).

the $e(\psi)$ wave functions can be regarded as linear combinations of the lowest unoccupied molecular orbitals of the NN ligand. Furthermore, the intensity of the low-energy shoulder can be used as a measure of the distortion away from D_{2d} symmetry. Conversely, as the more sterically demanding ligands impart more rigidity to the complex and enforce D_{2d} symmetry, the low-energy shoulder should decrease. On this basis, the strong shoulder appearing in the spectra of **2** can be interpreted as a flattening of the coordination sphere of copper(I). In **1**, the smaller ionic radius of the copper(II) ion allows an almost perfect planar arrangement of two o,o'-iPr$_2$C$_6$H$_3$-BIAN ligands around the copper centre with two phenyl groups that adopt face-to-face parallel positions (Fig. 3).

NMR Spectra of 2

From the literature it is known that aryl substituents with high steric demands (*ortho* substituents) have a lack of rotational freedom relative to the naphthalene backbone on the NMR time scale at room temperature and exhibit well-resolved signals [33]. Moreover, when this lack of rotational freedom is combined with interligand interactions, it complements the highly rigid coordination environment. Room temperature ^{1}H NMR spectra of **2** in CD$_2$Cl$_2$ and CDCl$_3$ clearly show quite broadened signals for the aromatic protons. Accordingly, the rigidity of **2** is low as compared to other [Cu(NN)$_2$]$^+$ systems [34]. This supports the view concerning the flattening phenomenon concluded from electronic spectra and electrochemical measurements.

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