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Synthesis and structural studies of diamagnetic first-row transition metal complexes with the rigid nitrogen ligand: bis[N-(2,6-diisopropylphenyl)imino]acenaphthene

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Dedicated to Professor Helmut Sigel on the occasion of his 65th birthday.

Abstract

Reported are the syntheses and characterization of diamagnetic copper(I) and iron(II) complexes with the bidentate nitrogen ligand bis[N-(2,6-diisopropylphenyl)imino]acenaphthene (o,o'-iPr₂C₆H₃-BIAN). Namely, they are [Cu(o,o'-iPr₂C₆H₃-BIAN)₂](ClO₄)(AcOH) (1), and [Fe(bipy)₂(o,o'-iPr₂C₆H₃-BIAN)](ClO₄)₂ (2), where bipy = 2,2'-bipyridine, AcOH = acetic acid. Moreover, the crystal structure of the novel dimeric Cu(I) compound with the *p*-brominated derivative of the o,o'-iPr₂C₆H₃-BIAN ligand, is also discussed. In [CuBr(o,o'-iPr₂-p-BrC₆H₂-BIAN)]₂ (3), the respective Cu(I) ion is in four-coordinate environment tetrahedrally surrounded by two imine nitrogen atoms of o,o'-iPr₂-p-BrC₆H₂-BIAN, and by two bridging bromide atoms. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: N-ligands; X-ray structures; Mixed-ligand complexes; Diamagnetic

1. Introduction

Mixed ligand complexes are observed in biological systems or in the intermediate chemical reactions with metal ions, which is important to understand the respective chemistry. Sigel's investigations concerning diimine and nucleoside mixed ligand chelate systems have a great help toward understanding the driving forces that led to the formation of such mixed-ligand complexes [1-3]. In the context of the ongoing industrial application of second- and third-row transition metal systems, for example, of rhodium, palladium and platinum, in catalytic processes [4], much interest has been focused on these metal complexes containing bulky rigid diimine ligands, such as bis(*N*-arylimino)ace-naphthene (Ar-BIAN) [5,6]. Along with this research,

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extensive synthetic work has also been reported. This includes novel complexes of the [Pd(Me)(p-An-BIAN)(L-L)]SO₃CF₃ type [7] [L-L = bis(anisylimino)acenaphthene (*p*-An-BIAN), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmphen), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3bis(diphenylphosphino)propane (dppp)], where, the p-An-BIAN ligand and a second L-L ligand are coordinated in a bidentate and unidentate fashion, respectively. Other interesting examples include the zero valent palladium and platinum [M(Ar-BIAN)(alkene)] complexes [8] with the bidentate Ar-BIAN or bis(phenylimino)camphane ligands obtainable only with electron poor alkenes, such as dimethyl fumarate, fumaronitrile, maleic anhydride, and tetracyanoethylene.

Except those systems with Ar-BIAN already mentioned above, up to now, only some rhenium complexes were reported [9]. Recently, first two copper(II) mixedligand complexes, namely [Cu(acac)(AcOH)(o,o'-

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iPr₂C₆H₃-BIAN)]ClO₄ and $[Cu(AcOH)Cl_2(o,o'$ $iPr_2C_6H_3$ -BIAN)] (where acac = acetylacetonate) were prepared and characterized in our laboratory [10]. Thus, in the present work, a further study on this field encompassing copper and iron transition metals and giving details of the spectroscopic, magnetic and structural features is presented. Here, we report the syntheses and characterization of some more copper and iron complexes, $[Cu(o,o'-iPr_2C_6H_3-BIAN)_2](ClO_4)(AcOH)_2$ (1), and $[Fe(bipy)_2(o,o'-iPr_2C_6H_3-BIAN)](ClO_4)_2$ (2). The X-ray crystal structure of the dimeric Cu(I) species with the *p*-brominated Ar-BIAN ligand, [CuBr(o,o' $iPr_2-p-BrC_6H_2-BIAN)_2$ (3), is discussed and compared with those previously reported [10].

2. Experimental

2.1. Material and instrumentation

All starting materials were purchased from Wako Pure Chemical Industries Ltd, and used without further purification. The o,o'-iPr₂C₆H₃-BIAN ligand was synthesized from acenaphthenequinone and 2,6-diisopropylaniline [10].

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 Series II CHNSIO Analyzer. Electronic spectra were recorded on an UV-3100PC Shimadzu spectrophotometer using 10 mm quartz cells at room temperature (r.t.). Powder reflectance spectra were obtained using the same instrument equipped with an integrating sphere and using BaSO₄ as a reference. Infrared spectra were recorded on a Perkin-Elmer FT IR Spectrometer Spectrum 2000 as KBr pellets and as Nujol mulls in the 4000-370 cm⁻¹ spectral range. Magnetic susceptibilities were measured at r.t. on a Shimadzu MB-100 Torsion Magnetometer. Diamagnetic corrections were calculated using Pascal's constants [11]. ¹H and ¹³C NMR measurements at 24, °C were run on a JEOL JNM LA 300 WB spectrometer at 300.40 and 75.45 MHz, respectively, using a 5 mm probe head in CD₂Cl₂ and CDCl₃ solvents. Chemical shifts are given in ppm relative to internal tetramethylsilane (TMS). A typical pulse width was 6.25 μ s for ¹H and 4.25 µs for ¹³C NMR measurements, respectively.

Thermogravimetric measurements were performed on a DTG-50 Shimadzu Instrument. Electrochemical measurements were recorded on a BAS 100BW electrochemical analyzer at r.t. with a scan rate of 100 mV s⁻¹. The solutions (1,2-dichloroethane (DCE), acetonitrile (ACN), and acetone (ACO)) contained 1 mM (where $M = mol dm^{-3}$) of the respective complex and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. A three-electrode configuration composed of a carbon working electrode, a platinum auxiliary electrode and a Ag/AgCl reference electrode was used. The ferrocene/ferrocenium couple served as an internal standard. The half wave potential $(E_{1/2})$ was calculated using the formula: $E_{1/2} = (E_{pa} + E_{pc})/2$, where, E_{pa} and E_{pc} are the peak anodic and peak cathodic potentials, respectively.

2.2. Synthesis of $[Cu(o,o'-iPr_2C_6H_3-BIAN)_2](ClO_4)(AcOH)_2$ (1)

Both 0.13 g $(3.51 \times 10^{-4} \text{ mol})$ of Cu(ClO₄)₂ 6H₂O and 0.35 g $(7.02 \times 10^{-4} \text{ mol})$ of $o, o' \cdot \text{iPr}_2\text{C}_6\text{H}_3\text{-BIAN}$ were combined and 40 ml of acetic acid was added. After 2 h stirring at r.t., the red–brown product was filtered, washed quickly with dichloromethane and dried in vacuum, yielding 58% of 1. C₇₆H₈₈ClN₄O₈Cu (1284.5): Calc. C, 71.06; H, 6.91; N, 4.36. Found: C, 71.04; H, 6.86; N, 4.59%. μ_{eff} (24 °C): diamagnetic. ¹H NMR (CD₂Cl₂, 300.40 MHz, 24 °C): $\delta = 1.05$ (d, H20), 1.27 (d, H21), 2.97 (sept, H19), 6.97 (d, H4), 7.43 (s, H15', H16', H17'), 7.45 (s, H15, H16, H17), 7.52 (pst, H5), 7.64 (pst, H5), 8.30 (d, H6). ¹³C NMR (CD₂Cl₂, 300.40 MHz, 24 °C): $\delta = 23.5$, 23.1 (C20, C21), 29.7 (C19), 125.1 (C15, C17), 125.5 (C4), 129.2 (C5), 129.9 (C6), 131.6 (C7), 139.2 (C14, C18), 144.9 (C12), 163.2 (C1).

2.3. Synthesis of $[Fe(bipy)_2(o,o'-iPr_2C_6H_3-BIAN)](ClO_4)_2$ (2)

A mixture of 0.27 g $(7.44 \times 10^{-4} \text{ mol})$ of Fe(II)(ClO₄)₂ 6H₂O, and 0.37 g (7.39 × 10⁻⁴ mol) of o,o'-iPr₂C₆H₃-BIAN in 40 ml of acetic acid was stirred for 15 min. To the red solid which formed soon from the red-brown solution, 0.23 g (1.48×10^{-3} mol) of 2,2'bipyridine was added directly. After 6 h stirring at r.t., the resulting red-brown solid product was filtered, washed quickly with dichloromethane and dried in vacuum, yielding 48% of **2**. $C_{56}H_{56}Cl_2N_6O_8Fe$ (1067.8): Calc. C, 62.98; H, 5.29; N, 7.87. Found: C, 62.70; H, 5.32; N, 7.96%. IR (bipy): 1575, 1607 cm⁻¹. $\mu_{\rm eff}$ (24 °C): diamagnetic. ¹H NMR (CD₂Cl₂, 300.40 MHz, 24 °C): $\delta = 1.00$ (d, H20), 1.21 (d, H21), 2.97 (sept, H19), 6.67 (d, H4), 7.28 (s, H15, H16, H17), 7.37 (pst, H5), 7.42 (d, bipy), 7.49 (pst, bipy), 7.90 (d, H6), 8.12 (pst, bipy), 8.48 (d, bipy). ¹³C NMR (CD₂Cl₂, 300.40 MHz, 24 °C): $\delta = 23.1$, 23.2 (C20, C21), 29.1 (C19), 123.5 (C16), 123.9 (C15, C17), 124.6 (C4), 128.3 (C5), 129.2 (C6), 130.0 (C3), 131.6 (C7), 135.5 (C14,18), 139.4 (bipy), 141.2 (C12), 148.0 (C13), 154.5 (bipy), 159.3 (bipy), 161.1 (C1).

(Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.)

2.4. Synthesis of $[CuBr(o,o'-iPr_2-p-BrC_6H_2-BIAN)]_2$ (3)

After dissolving o,o'-iPr₂C₆H₃-BIAN (0.30 g; 0.6 mmol) in a small amount of chloroform (99%), 18 ml of a chloroform-acetic acid solution (3:1) was added. This reaction mixture was heated to 60 °C and mixed with a methanol solution (5 ml) of CuBr₂ (0.07 g; 0.3 mmol). After heating to reflux, another 5 ml of methanol CuBr₂ solution (0.07 g; 0.3 mmol) was added and the mixture was stirred for 2 h at r.t. The product was isolated as a brown powder; yield: 69%, and purified by chromatography on silica gel using dichloromethane as eluent. Crystals suitable for the X-ray measurement were obtained directly from the mother liquor by free evaporation in air. C₃₆H₃₈Br₃N₂Cu (801.9): Calc. C 53.92, H 4.78, N 3.49%. Found. C 53.91, H 5.11, N 3.40%. UV–Vis (λ_{max}, nm; DCE): 480, 568 nm. μ_{eff} (24 °C): diamagnetic. ¹H NMR (CD₂Cl₂, 300.40 MHz, 24 °C): $\delta = 1.05$ (d, H20), 1.28 (d, H21), 2.97 (sept, H19), 6.80 (d, H4), 7.50 (pst, H5), 8.10 (d, H6). ¹³C NMR spectrum was not recorded due to low solubility.

2.5. X-ray data collection and structure refinement

Crystallographic data for complex **3** are summarized in Table 1. Crystal data were collected with a SMART/ RA CCD diffractometer (Mo K α radiation, graphite monochromator). The initial structure was solved by sIR92 [12] and refined by least-squares methods based on F^2 using SHELXL-97 [13]. Thermal ellipsoids (30% probability) and a molecular plot were drawn using the oRTEP-III program. The multi-scan empirical absorption correction ($T_{\min}/T_{\max} = 0.5575/1.0000$) was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined geometrically on their respective carrier atoms using three common isotropic thermal motion parameters (mixed treatment).

3. Results and discussion

3.1. Physical properties of Cu(I) and Fe(II) complexes with the $o_{,o'}$ -i $Pr_{2}C_{6}H_{3}$ -BIAN ligand

The physical data of all metal complexes are listed in Table 2 in which diamagnetism is observed in case of all the three studied complexes. Formation of the free o,o'-iPr₂C₆H₃-BIAN ligand can be confirmed from IR spectra where only C=N stretching vibrations are observed at 1671, 1652, 1642 cm⁻¹ [10], and no C=O stretching vibrations of the starting diketones in the 1700–1800 cm⁻¹ region. Moreover, these bands assigned to v(C=N) in free ligand are shifted to lower

Table 1 Crystallographic data for complex **3**

Crystal data	
Empirical formula	$C_{36}H_{38}Br_3CuN_2$
Formula weight	801.95
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.9939(2)
b (Å)	15.0192(2)
c (Å)	17.1426(2)
α, χ (°)	90.00
β (°)	78.47 (2)
V (Å ³)	3530.24(8)
Ζ	4
$D_{\rm calc} ({\rm g \ cm^{-3}})$	1.51
F(000)	1608
$\mu \text{ (mm}^{-1}\text{)}$	4.066
Crystal size (mm)	0.5 imes 0.2 imes 0.2
Data collection	
Temperature (K)	293(2)
θ Range (°)	1.72-27.45
Radiation	Mo Kα (Mon), 0.71069 Å
Scan mode	ω
Dataset	$-18 \le h \le 17; -19 \le k \le 18; -20 \le l \le 22$
Total data	23 383
Unique data	8010
Observed data	5157 $[I > 2.00\sigma(I)]$
Refinement	
Refined parameters	387
Final R, wR	0.0685, 0.1954

 $w = 1/[\sigma^2(F_0)^2 + (0.1152P)^2 + 7.7947P]$, where, $P = (F_0^2 + 2F_c^2)/3$.

wave numbers in the spectra of complexes thus indicating the coordination of both diimine nitrogen atoms of o,o'-iPr₂C₆H₃-BIAN to the metal center in all studied complexes (Table 2).

Generally, it is known that the aromatic rings with three adjacent free hydrogen atoms show strong bands in the $810-750 \text{ cm}^{-1}$ region due to the out-of-plane CH deformation vibrations [14]. Their position is determined almost wholly by their location on the ring rather than by the nature of the substituent and, with certain limitations, they provide an excellent method for recognition of the type of substitution. The very high intensity and sensitivity of these characteristic bands in this region make them particularly well suited for quantitative work, too. We noticed that splitting these out-of-plane CH deformation vibrations bands in the $810-750 \text{ cm}^{-1}$ region of complex 1 can be considered as a sign of the coordination of two Ar-BIAN ligands to the copper(I) ion.

In case of iron(II) complex **2**, two bands observed at 1575 and 1607 cm⁻¹ were assigned to v(C=N) vibrations of 2,2'-bipyridyl, which as a free molecule exhibits C=N vibration peaks at 1558 and 1580 cm⁻¹ [15]. A shift of these bands to higher wave numbers in IR spectra of complex **2** indicates the coordination of both nitrogen atoms of 2,2'-bipyridyl to the iron(II) center.

initiated (ciri) and electrochemical data of complexes at room temperature					
Complex	v(C=N)	v(ClO ₄ ⁻)	$E_{1/2}^{\ \ a}$	$\Delta E_{ m p}^{~~ m b}$	$\mu_{\rm eff}$ ^c
$\frac{[Cu(o,o'-iPr_2C_6H_3-BIAN)_2](ClO_4)(AcOH)_2 (1)}{[Fe(bipy)_2(o,o'-iPr_2C_6H_3-BIAN)](ClO_4)_2 (2)}$ $[CuBr(o,o'-iPr_2-p-BrC_6H_2-BIAN)] (3)$	1669, 1633 1669, 1649 1654, 1635	1116, 621 1090, 622	-0.31(DCE) -0.34(ACO) 0.73 (ACO), 0.76 (ACN)	173, 131 73, 84	Diam. Diam. Diam.

Infrared (cm⁻¹) and electrochemical data of complexes at room temperature

^a Half-wave potentials $E_{1/2}$ versus ferrocene/ferrocenium determined by cyclic voltammetry in DCE, ACN, or ACO at 100 mV s⁻¹ scan rate (electrolyte: 0.1 M Bu₄NClO₄).

^b $E_{\rm p} = (E_{\rm pa} - E_{\rm pc}), E_{\rm pa}$ and $E_{\rm pc}$ are the peak anodic and peak cathodic potentials, respectively.

^c Magnetic susceptibility, diam. = diamagnetic.

The strong band at around 1100 cm^{-1} and a sharp band at 622 cm⁻¹ suggest uncoordinated perchlorate anions [16] in complexes 1 and 2.

Electronic spectral data of complex 1 in various solvents and in the solid state are shown in Table 3. This complex absorbs in a broad region of the UV and visible spectra, showing very intense ligand-centered (LC) bands in the UV region and weaker metal-ligand charge-transfer bands (MLCT) in the visible region similar to those observed with other Cu(I) diimine systems [17]. Moreover, in the spectra of complex 1 in various organic solvents, there is a low-energy shoulder appearing in the 564-580 nm range. This shoulder has been attributed to result from a flattened distortion of the complex from D_{2d} symmetry as it was observed in the case of bis(phenanthroline)copper(I) complexes [18– 20]. This low-symmetry conformation likely occurs to maximize intra-molecular π -stacking interactions between opposing ligands. Thus, the intensity of the lowenergy shoulder can be considered as a rough measure of the distortion away from D_{2d} symmetry. On the basis of these considerations, it can be concluded that a significant 'flattening' distortion occurs about the copper ion in the MLCT state of $[Cu(o,o'-iPr_2C_6H_3 BIAN_2^+$.

The redox behavior of complex 1 was studied by cyclic voltammetry. It undergoes a quasi-reversible oneelectron oxidation process in 1,2-dichloroethane (DCE) and acetone (ACO) (Table 2), which can be attributed to the Cu(I) \leftrightarrow Cu(II) couple:

$$[Cu(o, o'iPr_2C_6H_3BIAN)_2]^{2+} + e^{-}$$

$$\leftrightarrow [Cu(o, o'iPr_2C_6H_3BIAN)_2]^{+}$$

T-1-1- 2

Moreover, except the Cu(I)/Cu(II) redox process

mentioned above, the voltammetric response of complex 1 between 1.3 and -0.8 V versus ferrocene/ferrocenium indicates the occurrence of chemical reactions coupled to the various electron transfers. Recently, a complex sequence of fragmentation steps has been proposed for related dimine systems under similar conditions [21]. A detailed investigation of such processes, however, was not attempted in the present study.

Low-spin iron(II) octahedral complexes are formed with ligands, which have a strong ligand field. The Ar-BIAN ligand satisfies such a requirement as we have succeeded to synthesize the diamagnetic [Fe(bipy)₂(o,o'iPr₂C₆H₃-BIAN)](ClO₄)₂ complex (**2**). The absorption spectrum of complex **2** shows three bands: 418 (the intra-ligand (IL) diimine transition), 479 and 600 nm (the MLCT transitions). However, this assignment must be regarded as tentative since low-spin iron(II) complexes present, are considerable assignment difficulties due to the strong intensities of bands in rather narrow range of wavelengths [22].

the Fe (II/III) couple was assessed by using cyclic voltammetry in various solvents. Based on peak-to-peak separation (ΔE_p), where, reversible behavior is commonly reported between 60 and 80 mV in organic solvents [22], complex 2 exhibited reversible redox behavior that appeared to progress from reversible in acetonitrile (ACO) to quasi-reversible in acetonitrile (ACN), see Table 2. No ligand reduction has been observed.

3.2. The synthesis and the structure of $[CuBr(o,o'-iPr_2-p-BrC_6H_2-BIAN)]_2$ (3)

During our attempt to synthesize the bromide analogue to the [Cu(AcOH)Cl₂(o,o'-iPr₂C₆H₃-BIAN)] com-

Table 3						
UV–Vis spectroscopic	data (λ_{max}	per nm)	of complex	1 at r	oom tempe	rature ^a

	(miax P)	F	r · · · · ·			
Solid	576 (sh)	480	458		360	
DCE	564 (sh)	494 (6000)	459 (8000)	435(7000)	368(8500)	
Chloroform	569 (sh)	458 (5500)	432 (6300)	405(5600)	376(5000)	
Toluene	580 (sh)	455 (1100)	425 (1300)		367(1500)	
THF	569 (sh)	460 (4200)	435 (4700)		367(6500)	

^a The extenction coefficient values are shown in parenthesis, sh = shoulder.

Table 2

Table 4

plex, an additional factor suddenly came into play. Bromination of the phenyl rings of o,o'-iPr₂C₆H₃-BIAN took place in the *para* position, as a result of the reduction of Cu(II) to Cu(I), which evidenced by the Xray analysis. This method can be considered as a new possible route of *p*-bromination of the phenyl group using Cu(II) bromide in organic chemistry.

An ORTEP plot showing the atomic numbering scheme is given in Fig. 1. Selected bond distances and angles are listed in Table 4. The copper(I) ion is tetrahedrally surrounded by the two nitrogen atoms N(1) and N(2) of o,o'-iPr₂-p-BrC₆H₂-BIAN, and by the two bromide atoms Br(1) and Br(1'). The copper atoms lie out of the Ar-BIAN ligand plane [C(13)N(1)C(1)C(2)N(2)-C(25)] by 0.79 Å.

Appraisal of the obtained structural data of complex 3 reveals some interesting features. Firstly, comparison of the bond lengths and angles in 3 with those of free bis(p-tolylimino)acenaphthene (p-Tol-BIAN) [10] shows some discrepancies that must result from the coordination to the copper atom and from the different aromatic groups on the imine N-atoms. These differences concern the imine C=N bonds, N(1)-C(1) and N(2)-C(2) of 1.287(6) and 1.283(6) Å, respectively, which are longer than those of the free (*p*-Tol-BIAN) ligand (1.267(3) Å). Due to its coordination to a metal, the bis(imino)acenaphthene moiety almost reaches planarity, as it is apparent from the torsion angles [N(2)-C(2)-C(1)- $N(1) = -0.2(7)^{\circ}$ and C(3)-C(2)-C(1)-C(11) = - $0.7(5)^{\circ}$]. In *p*-Tol-BIAN, the corresponding values are -6.5(3) and $-5.6(2)^{\circ}$. Secondly, compared with other two copper(II) complexes with o,o'-iPr₂C₆H₃-BIAN coordinated in a bidentate fashion and one copper(I)diimine complex, namely [Cu(acac)(AcOH)(o,o'-iPr₂C₆H₃-BIAN)]ClO₄, $[Cu(AcOH)Cl_2(o,o'-iPr_2C_6H_3-BIAN)]$ and $[CuBr(dmphen)]_2$ (dmphen = 2,9-dimethyl-1,10phenanthroline) [23], respectively. An increase in the Cu-N distance is apparent [the average Cu-N distances are 2.1114, 2.08445, 2.0702 and 2.0454 Å in 3, [CuBr(dmphen)]₂, $[Cu(AcOH)Cl_2(o,o'-iPr_2C_6H_3-$ BIAN)] and $[Cu(acac)(AcOH)(o, o'-iPr_2C_6H_3-BIAN)]$ -



Fig. 1. An ORTEP plot (30% probability level) of $[CuBr(o,o'-iPr_2-p-BrC_6H_2-BIAN)]_2$ (3).

complex b	
Cu(1)-N(1)	2.110(4)
Cu(1)-N(2)	2.112(4)
Cu(1)-Br(1)	2.3662(11)
Cu(1)-Br(1')	2.4791(11)
N(1)-C(1)	1.287(6)
N(1)-C(13)	1.452(6)
N(2) - C(2)	1.283(6)
N(2)-C(25)	1.441(6)
C(1)-C(2)	1.517(6)
C(2) - C(3)	1.476(7)
C(1) - C(11)	1.462(7)
N(1)-Cu(1)-N(2)	80.17(15)
N(1)-Cu(1)-Br(1)	118.66(12)
N(2)-Cu(1)-Br(1)	119.67(12)
Br(1)-Cu(1)-Br(1')	114.98(3)
Cu(1) - N(1) - C(1)	110.9(3)
Cu(1) - N(1) - C(13)	129.5(3)
Cu(1) - N(2) - C(2)	110.4(3)
Cu(1) - N(2) - C(25)	129.4(3)
C(1)-N(1)-C(13)	119.4(4)
C(2)-N(2)-C(25)	120.1(4)
C(30)-C(25)-N(2)-C(2)	-78.6(6)
C(18) - C(13) - N(1) - C(1)	84.7(6)
C(26)-C(25)-N(2)-C(2)	105.8(6)
C(14)-C(13)-N(1)-C(1)	-99.8(6)
C(2)-C(3)-C(12)-C(11)	-0.2(6)
C(3)-C(12)-C(11)-C(1)	-0.2(6)
N(2) - C(2) - C(1) - N(1)	-0.2(7)

ClO₄, respectively]. The bite angle N-Cu-N decreases in the following order: $81.81(5)^{\circ}$ in [Cu(acac)- $(AcOH)(o,o'-iPr_2C_6H_3-BIAN)]ClO_4,$ 80.36(8)° in 80.32 $[Cu(AcOH)Cl_2(o,o'-iPr_2C_6H_3-BIAN)],$ in $[CuBr(dmphen)]_2$ and $80.17(15)^\circ$ in 3. This decrease in the N-Cu-N angle is accompanied by bending of the aromatic groups on the imine N atoms more towards the copper center and away from the naphthalene backbone. The rigid naphthalene moiety and the aromatic groups with o- and p-substituents show no anomalies and the bond distances and angles are within the expected ranges [14].

-0.7(5)

4. Supplementary material

C(3)-C(2)-C(1)-C(11)

The crystallographic data of **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Center with the supplementary publication number 162037. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +441223-336-033; email: deposti@ccdc.cam.ac.uk or www:http.//www.cam.ac.uk).

Selected bond lengths (Å), angles (°), and torsion angles (°) for complex ${\bf 3}$

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