Mixed-Ligand Copper(II) Complexes with the Rigid Bidentate Bis(*N*-arylimino)acenaphthene Ligand: Synthesis, Spectroscopic-, and X-ray Structural Characterization

Adriana Paulovicova,[a] Usama El-Ayaan,[a,b] Koichi Shibayama,[c] Takeharu Morita,[c] and Yutaka Fukuda*[a]

Keywords: N ligands / Copper / X-ray crystal structures / Magnetic properties

Reported are the synthesis, characterization, and crystal structures of two mixed-ligand copper(II) complexes containing bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene (*o,o′*-*i*$Pr_2C_6H_3$-BIAN). In both complexes, namely [Cu(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)Cl_2] (**1**) and [Cu(acac)(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)](ClO_4) (**2**) (acac = acetylacetonate and AcOH = acetic acid), the copper ions are in a distorted square-pyramidal coordination environment with an acetic acid molecule in each apical position. The two imine nitrogen atoms of *o,o′*-*i*$Pr_2C_6H_3$-BIAN occupy the basal plane with the two chloride atoms and the two oxygen atoms of acac in complexes **1** and **2**, respectively. Complex formation results in certain structural changes inside the rigid N–N ligand. Such changes led to an increased planarity of the *o,o′*-*i*$Pr_2C_6H_3$-BIAN backbone, and produced a nearly perpendicular angle between the naphthalene and the aromatic imine planes. In complex **2**, the more perpendicular arrangement of the *o,o′*-diisopropylphenyl groups shielding the copper centre was structurally allowed by the elongation of one of the metal-to-ligand bonds and by the relatively larger N–Cu–N bite angle. Also discussed are IR, magnetic, and UV/Vis measurements.

Introduction

During the last decade there has been an increased interest in the use of bidentate and tridentate ligands in catalysis.[1−4] Recently, special attention has focused on the catalytic reactivity of late transition metals, for example, rhodium, palladium, and platinum, and their complexation with rigid bidentate ligands[5−9] such as bis(*N*-arylimino)acenaphthene (Ar-BIAN), which was first introduced by van Asselt and Elsevier in the early 1990s.[10] It has been shown that such metal systems containing Ar-BIAN are efficient catalysts in, for example, the homogeneous catalytic hydrogenation of alkynes,[11] in catalytic multi-component C−C coupling reactions,[10,12] and as models for co-polymerization or as catalysts in polymerization of alkenes.[13,14]

These (Ar-BIAN) ligands contain two conjugated imine functions, but they differ markedly from the commonly used diimine ligands such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). Firstly, the presence of two exocyclic imines, that are not part of the heteroaromatic ring system, is expected to lead to better σ-donating and π-accepting properties as compared to bpy and phen.[15−17] This property allows (Ar-BIAN) ligands to stabilize both the higher and lower oxidation states of the coordinated metal ions. Secondly, the rigidity of the acenaphthene backbone forces the imine *N*-atoms to remain in a fixed *cis* orientation, favouring the chelating coordination to a metal centre. Despite all the effort that has been put into the chemistry of rigid bidentate nitrogen ligands, there is a lack of available structural data. This is probably caused by the difficulties in growing single crystals for X-ray determination.

Our current interest is focused on the structural accommodation of bulky derivatives of 1,10-phenanthroline around the copper ion.[18] Therefore, we thought it would be reasonable to investigate coordination possibilities of such a huge, rigid ligand, namely bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene (*o,o′*-*i*$Pr_2C_6H_3$-BIAN) (Figure 1) when imposed on a copper centre. In this paper, we describe the isolation and full characterization, including X-ray structures, of two novel mixed-ligand copper(II) complexes, namely [Cu(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)Cl_2] (**1**), and [Cu(acac)(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$−BIAN)](ClO_4) (**2**).

[a] Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka,
Bunkyo-ku, Tokyo 112-8610, Japan
Fax: (internat.) + 81-3/5978-5137
E-mail: fukuda@cc.ocha.ac.jp
[b] Department of Chemistry, Faculty of Science, Mansoura University,
Mansoura 35516, Egypt
E-mail: usama@cc.ocha.ac.jp
[c] Sekisui Chemical Co., Ltd., 2-1 Hyakuyama, Shimamoto-cho, Mishima-gun,
Osaka 618-8589, Japan

Results and Discussion

Crystal-Structure Analysis of Complexes 1 and 2

[Cu(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)Cl_2] (1)

An ORTEP plot (30% thermal ellipsoids) showing the atomic-numbering scheme employed is given in Figure 2. This complex contains a distorted square-pyramidal cop-

  1434−1948/01/1010−2641 $ 17.50+.50/0

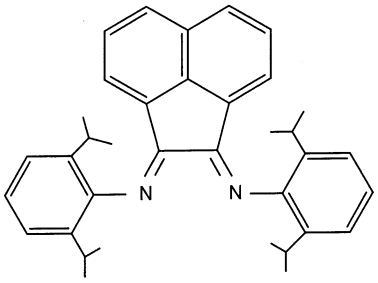

Figure 1. The structure of *o,o′*-*i*$Pr_2C_6H_3$-BIAN

per(II) moiety with two imine nitrogen atoms and two chloride atoms occupying the basal plane, as well as an acetic acid molecule in the apical site. This acetic acid ligand has the relatively longer bond length of 2.467(3) Å compared to those of the basal plane. X-ray analysis of complex **1** indicates that the imine C=N bonds N(1)−C(1) and N(2)−C(5) of 1.284(3) and 1.286(3) Å, respectively, are slightly longer than the standard N(sp^2)=C(sp^2) double bond (1.27 Å).[19] This is simply due to the coordination to the copper(II) centre. Upon coordination, a lowering of the strain in the naphthalene backbone occurs, which is indicated by the C(1)−C(5) bond shortening to 1.500(3) Å as compared to the corresponding bond length of 1.535(3) Å in case of free bis(*p*-tolylimino)acenaphthene (*p*-Tol-BIAN).[15] Torsion angels N(1)−C(1)−C(5)−N(2) of −0.3(3)° and C(2)−C(1)−C(5)−C(4) of −0.4(3)° reflect a planarity of the bis(imino)acenaphthene moiety. Angles between the planes of the naphthalene and aromatic N substituents are close to perpendicular (84°), and in good agreement with the corresponding angles of (84°) in [Pd(Me)Cl(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)][15] and (85°) in [Pd(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)(MA)][20] (MA = maleic anhydride), but larger than in [Pd(*p,p′*-$Me_2C_6H_3$-BIAN)(MA)][21] of (55°) and the free *p*-Tol-BIAN ligand of (61°). This must certainly be ascribed to the presence of *o*-isopropyl substituents rather than to the coordination to the metal ion.

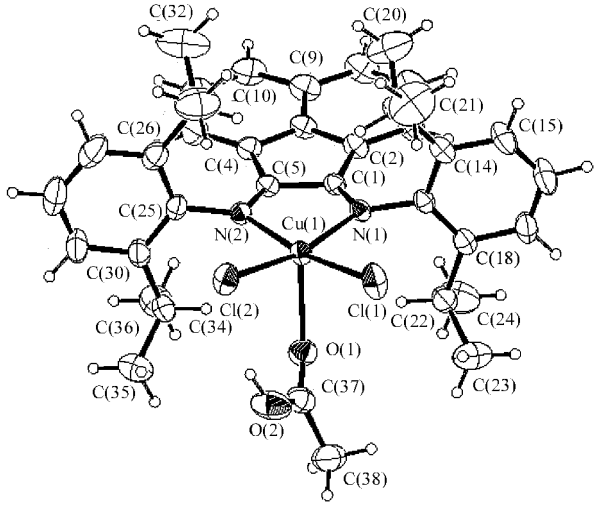

Figure 2. An ORTEP view of [Cu(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)Cl_2] (**1**)

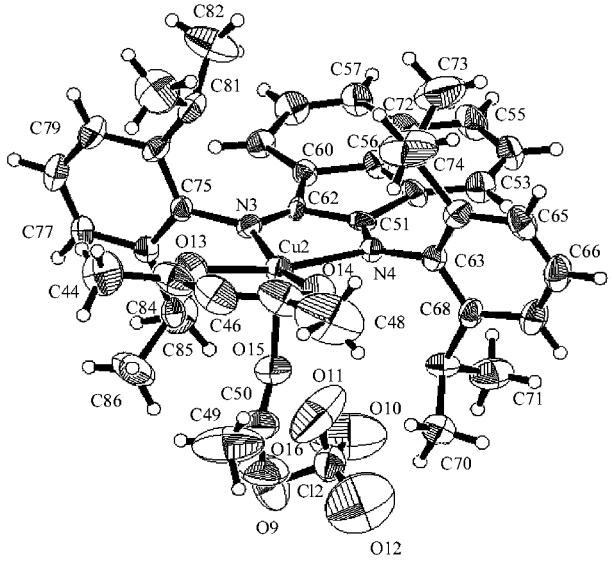

Figure 3. An ORTEP view of [Cu(acac)(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)]·(ClO_4) (**2**)

[Cu(acac)(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)]·(ClO_4) (2)

An ORTEP plot (30% thermal ellipsoids) showing the atomic-numbering scheme employed is given in Figure 3. The monodentate acetic acid, the bidentate acac, and (N−N) ligands coordinate to Cu^{II} to form a slightly-distorted square-pyramidal coordination geometry. Its basal plane contains two oxygen atoms of acac and two imine nitrogen atoms of *o,o′*-*i*$Pr_2C_6H_3$-BIAN, while the monodentate acetic acid is accommodated in the apical position. Selected bond lengths and angles of both complex **1** and **2** are given in Table 1.

The crystallographic asymmetry of complex **2** is clearly reflected by the different imine (N−C) bond lengths: N(3)−C(62) is 1.286(3) Å and N(4)−C(51) is 1.359(2) Å. A comparison with complex **1** shows a more planar bis(imino)acenaphthene skeleton as confirmed by the smaller torsion angles [N(3)−C(62)−C(51)−N(4) = 0.1(2)° and C(60)−C(62)−C(51)−C(52) = 0.3(2)°] and the rather shorter C(62)−C(51) bond length of 1.433(2) Å.

The *o,o′*-diisopropylphenyl groups are bent towards the naphthalene backbone, away from the copper centre, with nearly perpendicular angles between the planes of naphthalene and the aromatic imine. This approximately perpendicular arrangement of the *o,o′*-diisopropylphenyl groups in complex **2** shields the copper centre more effectively above and below the coordination plane. This extra shielding makes it difficult to accommodate the (acac) ligand within the basal plane. This problem is perfectly solved by the appropriate structural changes inside the *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand, namely by the elongation of N(4)−C(51) to 1.359(2) Å, and the larger bite angle N(3)−Cu(2)−N(4) of 82°, as compared to the corresponding angle of 80° in case of **1**. There is also a shortening of the C(62)−C(51) bond to 1.433(2) Å. Consequently, all these changes within the *o,o′*-

Table 1. Selected bond lengths [Å], angles [°], and torsion angles [°] for complexes **1** and **2**

1		**2**	
Cu(1)−N(1)	2.0561(19)	Cu(2)−N(3)	2.0153(14)
Cu(1)−N(2)	2.084(2)	Cu(2)−N(4)	2.0755(13)
Cu(1)−Cl(1)	2.2213(8)	Cu(2)−O(13)	1.8924(17)
Cu(1)−Cl(2)	2.2453(7)	Cu(2)−O(14)	1.8982(16)
Cu(1)−O(1)	2.467(3)	Cu(2)−O(5)	2.2721(13)
N(1)−C(1)	1.284(3)	N(3)−C(62)	1.286(2)
N(1)−C(13)	1.442(3)	N(3)−C(75)	1.480(2)
N(2)−C(5)	1.286(3)	N(4)−C(51)	1.359(2)
N(2)−C(25)	1.450(3)	N(4)−C(63)	1.422(2)
C(1)−C(5)	1.500(3)	C(62)−C(51)	1.433(2)
C(1)−C(2)	1.455(3)	C(62)−C(60)	1.442(2)
C(5)−C(4)	1.469(3)	C(51)−C(52)	1.505(2)
N(1)−Cu(1)−N(2)	80.36(8)	N(3)−Cu(2)−N(4)	81.81(5)
Cl(1)−Cu(1)−Cl(2)	95.58(3)	O(13)−Cu(2)−O(14)	94.87(7)
N(1)−Cu(1)−Cl(1)	91.30(6)	N(3)−Cu(2)−O(13)	90.98(7)
N(2)−Cu(1)−Cl(2)	91.63(6)	N(4)−Cu(2)−O(14)	90.42(6)
N(1)−Cu(1)−O(1)	95.4(1)	N(3)−Cu(2)−O(15)	93.36(7)
N(2)−Cu(1)−O(1)	94.6(1)	N(4)−Cu(2)−O(15)	94.33(7)
Cu(1)−N(1)−C(1)	112.92(15)	Cu(2)−N(3)−C(62)	114.96(11)
Cu(1)−N(1)−Cl(13)	129.00(15)	Cu(2)−N(3)−C(75)	129.14(11)
Cu(1)−N(2)−C(5)	112.27(17)	Cu(2)−N(4)−C(51)	107.03(11)
Cu(1)−N(2)−C(25)	127.41(16)	Cu(2)−N(4)−C(63)	128.17(10)
C(5)−N(2)−C(25)	119.8(2)	C(51)−N(4)−C(63)	124.59(14)
C(1)−N(1)−C(13)	117.66(19)	C(75)−N(3)−C(62)	115.78(14)
		O(13)−Cu(2)−O(15)	95.20(8)
		O(14)−Cu(2)−O(15)	97.83(9)
C(18)−C(13)−N(1)−C(1)	92.1(4)	C(76)−C(75)−N(3)−C(62)	86.7(2)
C(30)−C(25)−N(2)−C(5)	−98.5(4)	C(68)−C(63)−N(4)−C(51)	−87.0(2)
C(14)−C(13)−N(1)−C(1)	−87.8(4)	C(80)−C(75)−N(3)−C(62)	−94.60(19)
C(26)−C(25)−N(2)−C(5)	83.8(4)	C(64)−C(63)−N(4)−C(51)	92.6(2)
C(1)−C(2)−C(3)−C(4)	−0.2(3)	C(62)−C(60)−C(61)−C(52)	0.95(19)
C(2)−C(3)−C(4)−C(5)	−0.1(3)	C(51)−C(52)−C(61)−C(60)	−0.67(17)
N(1)−C(1)−C(5)−N(2)	−0.3(3)	N(3)−C(62)−C(51)−N(4)	0.1(2)
C(2)−C(1)−C(5)−C(4)	−0.4(3)	C(60)−C(62)−C(51)−C(52)	0.3(2)

i$Pr_2C_6H_3$-BIAN ligand led to one relatively long Cu(2)−N(4) distance of 2.0755(13) Å compared to the [Cu(2)−N(3) distance of 2.0153(14) Å]. Complex **2** with the structural index parameter value, τ, of 2.6% shows a more regular square-pyramidal geometry than complex **1** with a τ equal to 4.5%. According to Addison et al.,[22] τ should have a value of 0% for a perfect square-pyramid and 100% for a perfect trigonal pyramidal structure: $\tau = \{(\theta - \varphi)/60\} \times 100$, where θ and φ are the largest and the second largest basal angles, respectively.

The Cu−O(acac) distances, namely Cu(2)−O(13) = 1.8924(17) Å and Cu(2)−O(14) = 1.8982(16) Å, and the bite angle O(13)−Cu(2)−O(14) of 94.87(7)° are similar to the corresponding distances and bite angles observed in other mixed ligand copper(II) complexes containing the acac ligand.[18,23,24]

It is reasonable to make a structural comparison of complex **2** with the [Cu(acac)(dmph)(NO_3)] complex[18] (dmph = 2,9-dimethyl-1,10-phenanthroline). Namely, in the former complex, the two isopropylphenyl moieties allow only a planar coordination of the diimine, while in the latter, the methyl substituents that are in the same diimine plane prevent both N donors from occupying the basal plane together with the acac ligand (Figure 4).

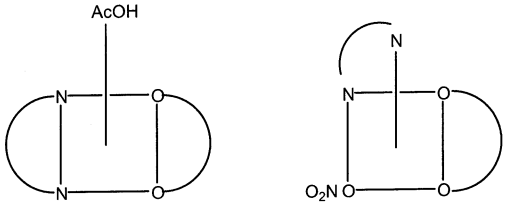

Figure 4. Schematic structures of complex **2** and [Cu(acac)(dmph)(NO_3)]

IR and UV/Vis Spectroscopy

Infrared spectroscopic data for the free *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand and both complexes **1** and **2** are listed in Table 2. Formation of the free *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand can be determined from the IR spectroscopy where only C=N stretching vibrations were observed in the 1642−1671 cm^{-1} range and no C=O stretching vibrations of the starting diketones in the 1700−1800 cm^{-1} region. The bands

assigned to ν(C=N) are shifted to lower wavenumbers in the complex formation indicating, the coordination of both diimine nitrogen atoms of *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand to the copper(II) ion. Strong bands observed in the 1695 and 1705 cm^{-1} regions for complex **1** and **2**, respectively, indicate the coordination of an acetic acid molecule.

Table 2. IR spectra (cm^{-1}) of *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand and complexes **1** and **2**

Compound	ν(C=N)	ν(ClO_4^-)	ν(AcOH)
o,o′-*i*$Pr_2C_6H_3$-BIAN	1671, 1652, 1642	–	–
Complex **1**	1661, 1635	–	1695
Complex **2**	1668, 1640	1110, 622	1705

IR spectra of complex **2** show two peaks, 1570 and 1519 cm^{-1}, that can be assigned to ν(C=O) and ν(C=C) of the acac ligands, respectively, consistent with those observed for [Cu(acac)$_2$].[25] The strong band observed at 1110 cm^{-1} (antisymmetric stretch) and the sharp band at 622 cm^{-1} (antisymmetric bend), suggest uncoordinated perchlorate anions[26] in agreement with the X-ray structure of **2**.

Solid-state room-temperature electronic spectra of **1** and **2** exhibit a broad d-d band at 700 and 625 nm, respectively, typical for square-pyramidal copper(II) complexes.[27−29] Another band appeared in the visible spectral region, 558 and 545 nm, of complexes **1** and **2**, respectively, assigned to the MLCT transitions from copper(II) to the π* orbitals of *o,o′*-*i*$Pr_2C_6H_3$-BIAN. This shift to much longer wavelength than those of other diimine ligands can be explained on the basis that the *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand provides π* orbitals at rather low energies[17,30,31] that results in the increased overlap with the metal d orbitals. Consequently, this results in a stronger π-bonding interaction accompanied by a red-shift of the MLCT transition. Electrochemical studies[32] on the π-acceptor properties of the bis(arylimino) acenaphthene reveal a much larger positive potential than those of other diimine ligands confirming the larger π-acceptor strength of bis(arylimino)acenaphthene.

Absorption spectra of both complexes show various bands below 420 nm that can be assigned to intraligand transitions of the free diimine ligand, which absorbs in the same spectral region. Electronic spectra were also recorded in solution using a variety of solvents (DCE, THF, toluene, and chloroform). All solution spectra of both complexes **1** and **2** are very similar to the corresponding solid-state spectra.

Conclusion

From the X-ray structure analysis of both copper(II) complexes **1** and **2** we can conclude that the two diisopropylphenyl moieties on the imine nitrogens of the *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand are flexible and show no conjugation with the naphthalene-diimine backbone. We have shown the difference in the coordination behaviour of this ligand when bound to the copper(II) ion. In complex **1**, a common equal-in-length bidentate coordination of *o,o′*-*i*$Pr_2C_6H_3$-BIAN was observed. In complex **2**, the pronounced shielding effect introduced by the *o,o′*-diisopropylphenyl groups, resulting from the more perpendicular arrangement, was identified by the relatively longer (Cu−N) bond, and by the respective changes inside the *o,o′*-*i*$Pr_2C_6H_3$-BIAN ligand. UV/Vis absorption spectra of both complexes indicate a strong π-back-bonding and a smaller HOMO−LUMO energy gap.

Experimental Section

Materials and Instrumentation: All chemicals were purchased from the Wako Pure Chemical Industries Ltd., and used without further purification.

Elemental analyses (C, H, N) were performed on a PE 2400 Series II CHNS/O Analyzer. − 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 instrument equipped with an integrating sphere and using $BaSO_4$ as a reference. − Infrared spectra were recorded on a Perkin−Elmer FT-IR Spectrometer Spectrum 2000 in a KBr pellet and as a Nujol mull in the 4000−370 cm^{-1} spectral range. − Magnetic susceptibilities were measured at room temperature on a Shimadzu MB-100 Torsion Magnetometer. Diamagnetic corrections were considered by using Pascal's constants.[33] − Thermogravimetric measurements were performed on a DTG-50 Shimadzu instrument. − ^1H and ^{13}C NMR spectra were run on a JEOL JNM LA 300 WB spectrometer at 300.40 and 75.45 MHz, respectively, using a 5 mm probe head. CD_2Cl_2 and $CDCl_3$ were used as a solvent. Chemical shifts are given in ppm relative to the internal TMS standard. The typical pulse width was 6.25 μs for ^1H and 4.25 μs for ^{13}C measurements. Assignment of the ^{13}C signals based on ref.[15] was confirmed by off-resonance decoupled and DEPT-135 measurements.

Synthesis of [*N*-(2,6-Diisopropylphenyl)imino]acenaphthene: This ligand was prepared using a method different to that published by Asselt, Elsevier et al.[15] Acenaphthenequinone (1.35 g, 7.4 mmol) in 65 mL of acetonitrile was heated under reflux (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 a 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. Yield 3.15 g (85%). − $C_{36}H_{40}N_2$ (500.7): calcd. C 86.35, H 8.05, N 5.60; found. C 85.85, H 8.03, N 5.34%. − ^1H NMR ($CDCl_3$, 300.40 MHz, 24 °C): δ = (0.97 d, 15-H), 1.23 (d, 16-H), 3.03 (sept, 14-H), 6.63 (d, 3-H), 7.26 (s, 12-H, 11-H, 10-H), 7.36 (pst, 4-H), 7.88 (d, 5-H). − ^{13}C NMR (CD_2Cl_2, 300.40 MHz, 25.4 °C): δ = 23.1 (C-16), 23.2 (C-15), 29.1 (C-14), 123.5 (C-11), 123.9 (C-10, C-12), 124.6 (C-3), 128.3 (C-4), 129.2 (C-5), 130.0 (C-2), 131.6 (C-6), 135.5 (C-9, C-13), 141.2 (C-7), 148.0 (C-8), 161.1 (C-1).

Synthesis of [Cu(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)Cl_2] (1): Bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene, *o,o′*-*i*$Pr_2C_6H_3$-BIAN, (0.35 g, 0.7 mmol) was dissolved in a small amount of chloroform (99%). A mixture of chloroform/acetic acid (15 mL, the 2:1 ratio) was then added, and the solution was heated for 10 min at 60 °C. Subsequently, a methanolic solution (7 mL) of $CuCl_2 \cdot 2H_2O$ (0.12 g, 0.7 mmol) was added dropwise to the *o,o′*-*i*$Pr_2C_6H_3$-BIAN solu-

tion. This mixture was then stirred for 2 h at room temperature. After 2 days of slow evaporation in air, dark-green prism-shaped crystals formed and were suitable for the single X-ray measurement. Yield 0.39 g (80%). − $C_{38}H_{44}Cl_2CuN_2O_2$ (695.20): calcd. C 65.65, H 6.38, N 4.03; found. C 66.30, H 6.35, N 3.95%. μ_{eff}: 2.0 B.M. (19 °C).

Synthesis of [Cu(acac)(AcOH)(*o,o′*-*i*$Pr_2C_6H_3$-BIAN)]·(ClO_4) (2): Two preparation methods were used.

Method A: To a suspension of 0.26 g (0.7 mmol) of $Cu(ClO_4)_2·6H_2O$ and 0.35 g (0.7 mmol) of *o,o′*-*i*$Pr_2C_6H_3$-BIAN in 15 mL of AcOH, 0.07 mL (0.7 mmol) of acetylacetonate was added directly and the mixture was stirred at room temperature. After 3 hours the microcrystalline product precipitated from the dark green solution. This solid was filtered, washed with cyclohexane and dried in air. The yield of the green micro-crystals was 0.48 g (82%). − $C_{43}H_{51}ClCuN_2O_8$ (822.86): calcd. C 62.76, H 6.25, N 3.41; found C 62.55, H 6.33, N 3.58%. μ_{eff}: 1.7 B.M. (24 °C).

Method B: (The same amounts were used as in method A). Acetylacetonate was added directly to a methanolic solution (5 mL) of $Cu(ClO_4)_2·6H_2O$. This mixture was stirred (while heating) for 10 min. A hot 2:1 chloroform/acetic acid solution (10:5 mL) of *o,o′*-*i*$Pr_2C_6H_3$-BIAN was then added. The resulting clear (i.e. no solid) green solution was stirred for 1 h and left to stand in air. After 3 days, needle-shaped and prism-shaped crystals appeared, both of which were suitable for X-ray measurements. Data were collected from a needle-shaped single crystal. − Elem. anal. found: C 61.82, H 6.26, N 3.36%.

Table 3. Crystal data, data collection, and structure refinement for complexes **1** and **2**

	1	**2**
Crystal data		
Formula	$C_{38}H_{44}Cl_2CuN_2O_2$	$C_{43}H_{51}ClCuN_2O_8$
Molecular mass	695.23	822.84
Crystal system	Orthorhombic	Orthorhombic
Space group	*P*21 21 21	*Pba*2
a [Å]	12.1400(6)	21.7710(2)
b [Å]	13.2140(6)	21.7780(3)
c [Å]	23.1620(5)	18.66700(10)
α, β, χ [°]	90.00	90.00
V [Å^3]	3715.6(3)	8850.56(15)
Z	4	8
$D_{calcd.}$ [g·cm^{-3}]	1.326	1.363
μ [cm^{-1}]	13.19	6.12
Crystal size [mm]	0.35×0.25×0.13	0.50×0.45×0.25
Data collection		
Temperature [K]	298	293
θ range [°]	1.08−27.98	1.09−27.46
Radiation	Mo-K_α (Mon), 0.71073 Å	Mo-K_α (Mon), 0.71069 Å
Scan mode	Image Plate	ω
Data set	$-15 \le h \le 16$; $-17 \le k \le 17$; $-29 \le l \le 29$	$-28 \le h \le 19$; $-28 \le k \le 27$; $-24 \le l \le 23$
Total data	8650	59497
Unique data	8630	19854
Observed data	7836 [$I > 2.00\sigma(I)$]	13207 [$I > 2.00\sigma(I)$]
Refinement		
Refined parameters	407	1014
Final *R*, w*R*	0.0476, 0.1365	0.0608, 0.1552

X-ray Structure Determination of 1 and 2: Crystallographic data for both complexes are summarized in Table 3. Single crystals of **1** and **2** were obtained directly from a chloroform/acetic acid solution. Crystal data for complex **1** were collected (Mo-K_α radiation, graphite monochromator) with a Mac Science DIP2030 K diffractometer. While for complex **2**, a SMART/RA CCD diffractometer was used. Accurate unit cell parameters and orientation matrices were determined by a least-squares refinement of setting angles of a set of well-centred reflections. An Image Plate for **1** and ω scan method for **2** were used. In both cases, the initial structure was solved by SIR92[34] and refined by least-squares methods based on F^2 using SHELXL-97.[35] Thermal ellipsoids (30% probability) and molecular plots were drawn using the maXus (MacScience) and ORTEP programs, for **1** and **2**, respectively. Absorption corrections were applied by multiscan (T_{min}/T_{max} of 0.691:0.740) for **1** and SADABS[36] (T_{min}/T_{max} of 0.829:1.000) for **2**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at calculated positions and refined while riding on their respective carrier atoms using three common isotropic thermal motion parameters (constrained for **1**, and mixed treatment for **2**).

Since the space groups of both complexes are polar, it was necessary to use the Flack absolute structure parameter,[37] which refined to $x = 0.056(13)$ in **1** and to $x = 0.00$ in **2**. There were two independent molecules in the asymmetric unit of complex **2**. The crystallographic data for both structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-158181 and CCDC-158307 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was partly supported by a Grand-in-Aid (Scientific Research No. 11304046) from the Ministry of Education, Science, Culture and Sports of Japan. Usama El-Ayaan thanks the Ochanomizu University for supporting his stay in Japan. Authors are grateful to Prof. Yuji Ohashi and Ms. Champika Vithana, Tokyo Institute of Technology, for their help with the X-ray structure determinations.

[1] C. Botteghi, G. Chelucci, G. Chessa, G. Delogu, S. Gladiali, F. Soccolini, *J. Organomet. Chem.* **1986**, *304*, 217−225.
[2] M. E. Wright, S. A. Svejda, M.-J. Jin, M. A. Peterson, *Organometallics* **1990**, *9*, 136−146.
[3] H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, *Organometallics* **1991**, *10*, 500−508.
[4] U. Leutenegger, G. Umbricht, C. Fahrni, P. von Matt, A. Pfaltz, *Tetrahedron* **1992**, *48*, 2143−2156.
[5] J. H. Groen, C. J. Elsevier, K. Vrieze, W. J. J. Smeets, A. L. Spek, *Organometallics* **1996**, *15*, 3445−3455.
[6] J. H. Groen, J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, *Organometallics* **1997**, *16*, 68−77.
[7] J. G. P. Delis, J. H. Groen, K. Vrieze, P. W. N. M. van Leeuwen, N. Veldman, A. L. Spek, *Organometallics* **1997**, *16*, 551−562.
[8] J. H. Groen, M. J. M. Vlaar, P. W. N. M. van Leeuwen, K. Vrieze, H. Kooijman, A. L. Spek, *J. Organomet. Chem.* **1998**, *551*, 67−79.
[9] R. A. Klein, P. Witte, R. van Belzen, J. Fraanje, K. Goubitz, M. Numan, H. Schenk, J. M. Ernsting, C. J. Elsevier, *Eur. J. Inorg. Chem.* **1998**, 319−330.

[10] R. van Asselt, C. J. Elsevier, *Organometallics* **1992**, *11*, 1999−2001.
[11] M. W. van Laren, C. J. Elsevier, *Angew. Chem. Int. Ed.* **1999**, *38*, 3715−3717.
[12] R. van Belzen, H. Hoffmann, C. J. Elsevier, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1743−1745.
[13] R. van Asselt, E. E. C. G. Gielens, R. E. Rülke, K. Vrieze, C. J. Elsevier, *J. Am. Chem. Soc.* **1994**, *116*, 977−985.
[14] L. K. Johnson, C. M. Kilian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.
[15] R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, *Recl. Trav. Pays-Bas* **1994**, *113*, 88−98.
[16] K. J. Cavell, D. J. Stufkens, K. Vrieze, *Inorg. Chim. Acta* **1980**, *47*, 67−76.
[17] J. Reinhold, R. Benedix, P. Birner, H. Hennig, *Inorg. Chim. Acta* **1979**, *33*, 209−231.
[18] A. Paulovicova, U. El-Ayaan, Y. Fukuda, *Inorg. Chim. Acta*, in press.
[19] M. Burke-Laing, M. Laing, *Acta. Crystallogr., Sect. B* **1976**, *32*, 3216−3224.
[20] R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, *Inorg. Chem.* **1994**, *33*, 1521−1531.
[21] H. Kooijman, A. L. Spek, R. van Belzen, C. J. Elsever, *Acta Crystallogr., Sect. C* **1997**, *53*, 1593−1596
[22] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349−1356.
[23] C.-C. Su, S.-P. Wu, C.-Y. Wu, T.-Y. Chang, *Polyhedron* **1995**, *14*, 267−275.
[24] N. A. Bailey, D. E. Fenton, M. V. Fracklin, M. Hall, *J. Chem. Soc., Dalton Trans.* **1980**, 984−990.
[25] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fourth ed., Wiley-Interscience, New York, **1986**.
[26] P. Chaudhuri, M. Winter, U. Flörke, H.-J. Haupt, *Inorg. Chim. Acta* **1995**, *232*, 125−130.
[27] L. P. Battaglia, A. C. Bonamartini, S. Ianelli, M. A. Zoroddu, G. Sanna, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3863−3867.
[28] H. Adams, N. A. Bailey, I. K. Campbell, D. E. Fenton, Q.-Y. He, *J. Chem. Soc. Dalton Trans.* **1996**, 2233−2237.
[29] M. M. Whittaker, W. R. Duncan, J. W. Whittaker, *Inorg. Chem.* **1996**, *35*, 382−386.
[30] A. J. Lees, *Chem. Rev.* **1987**, *87*, 711−743.
[31] D. J. Stufkens, *Coord. Chem. Rev.* **1990**, *104*, 39−112.
[32] G. Knör, M. Leirer, T. E. Keyes, J. G. Vos, A. Vogler, *Eur. J. Inorg. Chem.* **2000**, 749−751.
[33] E. König, *Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds*, Springer-Verlag, Berlin, **1966**
[34] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[35] *SHELXL-97*, *Program for the Refinement of Crystal Structures*, **1997**, G. M. Sheldrick, Univ. of Göttingen, Germany.
[36] *SADABS Program*, **1996**, G. M. Sheldrick, Univ. of Göttingen, Germany.
[37] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.

Received February 26, 2001
[I01064]