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Note

Synthesis, crystal structure and charge transfer spectra of dinuclear copper(I) complexes bearing 1,2-bis(arylimino)acenaphthene acceptor ligands

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Dedicated to Professor Wolfgang Kaim on the occasion of his 60th birthday.

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ABSTRACT

A series of dinuclear halide bridged copper(I) complexes with a central $[Cu_2(\mu-X)_2]$ diamond core (X = Cl, Br and I) and substituted bis(imino)acenaphthene (BIAN) ligands acting as strong π -acceptor subunits was prepared and characterized by elemental analysis, X-ray crystallography and various spectroscopic techniques. In the visible spectral range, the electronic spectra of these deeply colored air-stable compounds are dominated by low-lying charge transfer (CT) transitions. The corresponding broad absorption bands display a bathochromic shift and a decreasing amount of negative solvatochromism in the series X = Cl, Br and I. At the same time, the distance between the two metals becomes shorter and reaches the range of cuprophilic interactions. These systematic trends are interpreted as a decreasing amount of charge transfer character and a more pronounced delocalization between the two copper centers within in the same series.

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1. Introduction

Copper is a versatile redox-active bioelement, which can adopt a variety of different functions and coordination environments in metalloproteins [1,2]. The development of synthetic model systems for substrate transformations catalyzed by copper enzymes is therefore a very active research field in bioinorganic and biomimetic chemistry [3–5]. Among several other possibilities, the formation of dinuclear copper complexes coupled by bridging ligands represents a prominent structural motif in the active sites of many native metalloenzymes. The bioinorganic chemistry of such dicopper centers includes the activation and transport of dioxygen, the controlled hydroxylation of aromatic substrates, and the acceleration of typical mono-oxygenase reactions such as the selective oxidation of methane to methanol [2,6,7].

Since the corresponding redox processes are also very attractive in the context of green chemistry and technology, there is an increasing interest in the development of novel synthetic catalyst systems based on cheap, abundant and environmentally benign metal ions such as copper [8,9]. We have started to explore this possibility and selected the combination of copper(I) sites with 1,2-bis(arylimino)acenaphthene (Ar–BIAN) derivatives as redoxactive *N*-donor chelates [10–14]. The corresponding mononuclear systems are characterized by low-lying metal-to-ligand charge transfer (MLCT) transitions and display readily tuneable excited state properties, which makes them promising candidates for several applications including multielectron transfer photocatalysis and dye-sensitized solar cells [10]. Here, we wish to report the synthesis, structural characterization and spectroscopic properties of a series of novel air-stable dinuclear copper(I) complexes of the type $[(Ar-BIAN)CuX]_2$ (X = Cl, Br and I) with Ar = o,o'-bis(isopropyl) phenyl.

2. Results and discussion

2.1. Syntheses, characterization and crystal structures

Reaction of the 1,2-bis(o,o'-bis(isopropyl)phenylimino)acenaphthene with CuX leads to almost black, in diluted solution violet colored compounds, which are obtained in high yields as crystalline materials upon precipitation with *n*-pentane (Scheme 1). All metal complexes were stable in the solid state with respect to air and moisture. They were characterized by elemental analysis and ¹H NMR, FTIR and ESI-MS spectroscopic methods. The ¹H NMR spectra of **1** and **2** are very similar and feature broad signals for the alkyl and aromatic protons reflecting a fluxional behavior in solution. In contrast, the proton spectrum of **3** is well resolved (see Section 3). Upon coordination, the IR-band assigned to stretching vibrations of the imine C=N bonds is shifted to lower wavenumbers from 1671, 1652 and 1642 cm⁻¹ [15] for the free ligand to ~1645 cm⁻¹ for the copper complexes.

Single crystals suitable for X-ray diffraction of compounds **1–3** obtained from dcm/*n*-pentane are isomorphous and crystallize in



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Scheme 1.

Table 1

the monoclinic space group $P2_1/n$ (Z = 2). The asymmetric unit consists of the moiety [(BIAN)CuX]. Two Cu(I) atoms are bridged by two halide ions forming the planar rhombic $Cu_2(\mu-X)_2$ core. Additionally coordinated by the imine nitrogen atoms of the BIAN ligand, each Cu atom is in a distorted tetrahedral geometry. With increasing size of the halide anion the X-Cu-X angle is significantly increasing from 105.74(3)° to 119.61(2)° whereas the Cu-X-Cu angle decreases from $74.26(3)^{\circ}$ to $60.39(2)^{\circ}$. As a result, the copper atoms are coming closer together. The Cu-Cu distances of the chloride [2.772(1)Å] and bromide [2.753(1)Å] compounds are only slightly shorter than the sum of the van der Waals radii of two copper atoms (2.80 Å [16]). For the iodide compound the Cu-Cu separation of 2.588(1) Å lies within the range of "cuprophilic" interactions and is comparable to similar iodide complexes (2.530-2.612 Å [17-24]). The Cu-N distances are almost unaffected by changing the halide ligands and the bite angles of the BIAN ligand in compounds 1-3 are nearly identical (N-Cu-N \sim 80°) and similar to other Cu–BIAN complexes [10–14]. The crystal structure of the chloro bridged complex **1** is shown in Fig. 1. Characteristic bond lengths and angles for all three compounds are summarized in Table 1.

2.2. Electronic spectra

The absorption spectra of all copper(I) Ar–BIAN complexes investigated in this study display a series of electronic transitions below 370 nm and additional broad chromophoric features in the visible spectral region (Fig. 2, Table 2). The structured bands at shorter-wavelengths are assigned to intraligand (IL) transitions involving the conjugated π -electron system of the 1,2-diimine



Fig. 1. Molecular structure of 1 (ORTEP, displacement ellipsoids at the 50% probability level, H atoms are omitted for clarity).

Table 1			
Bond lengths	and	angles	of 1-3

	1	2	3
Bond length (Å)			
Cu1-Cu1	2.772(1)	2.753(1)	2.588(1)
Cu1-N1	2.102(1)	2.103(3)	2.114(3)
Cu1-N2	2.126(1)	2.117(3)	2.110(3)
Cu1-X1	2.274(1)	2.391(1)	2.553(1)
Cu1-X1	2.319(1)	2.428(1)	2.593(1)
N1-C1	1.290(3)	1.288(4)	1.280(4)
N2-C2	1.280(3)	1.276(4)	1.287(4)
Bond angles (°)			
N1-Cu1-N2	80.7(1)	80.0(1)	80.3(1)
X1-Cu1-X1 ⁱ	105.74(3)	110.31(2)	119.61(2)
Cu1-X1-Cu1 ⁱ	74.26(3)	69.69(2)	60.39(2)
N1-Cu1-X1	119.2(1)	117.8(1)	113.2(1)
N2-Cu1-X1	119.1(1)	117.0(1)	116.3(1)



Fig. 2. Electronic absorption and emission spectra of the [(Ar–BIAN)CuX]₂ compounds **1–3** in DCM solution (X = Cl, Br and I; λ_{exc} = 350 nm).

fragments, which are only slightly shifted with respect to the corresponding UV-absorptions of the free ligand [10].

Upon excitation of the complexes **1–3** in the UV spectral region, a weak luminescence with a maximum at around 510 nm could be observed (Fig. 2). This emission shows in the case of **1** and **3** a well-

 Table 2

 UV-Vis spectroscopic data of the complexes 1–3 in DCM solution at 298 K.

	λ_{\max} (nm) (ε (L/(mol cm))
1	408 (13 600), 341 sh (23 900), 326 (27 800), 311 sh (24 600), 270 (51 800), 259 (69 000)
2	424 (6800), 340 <i>sh</i> (12 400), 326 (15 000), 307 <i>sh</i> (13 000), 271 (26 700), 257 (38 100)
3	434 (12 600), 341 <i>sh</i> (22 200), 323 (28 500), 318 <i>sh</i> (28 500), 274 (38 800), 259 (59 400)

resolved vibronic pattern attributed to skeleton vibrations of the aromatic ligand system. Similar luminescence properties have been reported for aromatic molecules such as decacyclene [25] also containing the 14π -electron chromophore substructure of the Ar-BIAN system investigated in our work. Therefore we ascribe this feature of compounds **1–3** to an intraligand (IL) fluorescence. This tentative assignment is also supported by the facts that the free base Ar-BIAN ligand also luminesces under identical conditions (Fig. S1, Supplementary material), and that a similar emission behavior has been reported recently for zinc complexes carrying a related ligand system [26]. Further, much more detailed investigations, however, will be necessary to confirm this tentative assignment of the observed emission properties as an IL-type luminescence.

The additional bands of the copper complexes 1-3 in the visible spectral region are caused by the presence of charge transfer transitions. Mononuclear copper(I) systems carrying an individual Ar–BIAN π -acceptor subunit with Ar = 0,0'-bis(isopropyl)phenyl display a broad band maximum at 405 nm with an extinction coefficient of 7500 L/mol cm in DCM, which has been assigned in previous work as a metal-to-ligand charge transfer (MLCT) transition [10]. In analogy to these results, the broad chromophoric visible bands of the chloride-bridged complex 1 (Fig. 2) are ascribed to charge transfer transitions from predominately copper(I) localized d-electrons to the lowest unoccupied π^* -orbitals of the Ar–BIAN ligands. The observed band maximum and intensity of these MLCT transitions in 1 (Table 2) closely matches the features that could be expected for the presence of two independent mononuclear copper(I)-BIAN chromophores within the same molecule. It is therefore plausible to assume that the ground state electronic coupling and delocalization between the two individual halide bridged copper(I) subunits is not very pronounced in the case of the chloride complex **1**. Since the π -acceptor properties of 1,2-diimine ligands of the Ar-BIAN type are readily fine-tuned by variations of their aryl-substituents, it is possible to control the excitation energy of such MLCT states over a wide spectral range. For example, a significant red-shift of approximately 5400 cm⁻¹ can be predicted for the corresponding Ar-BIAN systems carrying Ar = methoxyphenyl instead of the o,o'-bis(isopropyl)phenyl substituents selected for the present investigation [10,27].

Compared to the chloride bridged derivative **1**, the maxima of the charge transfer transitions in the bromide and iodide bridged complexes **2** and **3** systematically shift to longer wavelengths (Fig. 2), which is in agreement with the regular variations in electronegativity.

The simplified picture of a predominant MLCT nature of the charge transfer bands in the dinuclear $[(Ar-BIAN)CuX]_2$ compounds, however, has to be gradually modified in the series X = Cl, Br and I. In the bromide compound **2** and especially in the case of the iodide complex **3**, the orbital parentage of the lowest-lying excited states is no longer unambiguously settled. Due to the more reducing character of the bridging ligands X in **2** and **3**, the occurrence of ligand-to-ligand charge transfer (LLCT) transitions from the halide lone-pairs to the π^* -orbitals of the diimine



Fig. 3. Correlation between the charge transfer transition energies of compounds **1** (**■**), **2** (**●**) and **3** (**▲**) with the E^*_{MLCT} values [27] of different solvents.

acceptor ligand has to be taken into consideration. Moreover, a variation of the bridging halide ligands X has a significant effect on the Cu...Cu distances and the Cu-X-Cu angles of the central $Cu_2(\mu-X)_2$ core of the three complexes (Table 1). These parameters are well known to strongly influence the exchange interactions in dinuclear ligand bridged copper systems [28]. Thus they could also modulate the properties of the charge transfer bands observed in our compounds by a significant mixing of the transitions with copper(I)to-diimine (MLCT) and halide-to-diimine (LLCT) character accompanied by an increasing electronic delocalization in the series X = Cl, Br and I. In order to support such a hypothesis, we also studied the typical negative solvatochromism of the complexes 1-3, shifting the visible absorption maxima of all three compounds to higher energy with increasing solvent polarity. The degree of this characteristic effect can be quantified by applying different solvent polarity scales such as the empirical E^*_{MLCT} -parameters [29] shown in Fig. 3.

A reasonably linear correlation is observed for the solvatochromic behavior of all compounds investigated.¹ The slopes of the regression line are 6.0×10^3 , 3.4×10^3 and 1.4×10^3 cm⁻¹ for X = Cl, Br and I, respectively. These data reflect a rather strong effect of the different halide bridges on the dipole moment changes induced upon excitation in the charge transfer region, which strongly indicates that the dominant MLCT character in the chloride bridged system 1 changes into an almost solvent independent transition between delocalized frontier orbitals in the case of the iodide complex 3. The bromide derivative 2 represents an intermediate situation, which conserves a significant degree of charge transfer character in the lowest-lying excited states. Therefore the effects of different bridging atoms X together with the possibility of tuning the π -acceptor properties of the Ar–BIAN ligands by variations of the aryl substituents offers a versatile tool to chemically modify and control the absorption characteristics and excited state reactivity patterns of dinuclear copper(I) BIAN complexes and related systems. This should be a very useful property in terms of many potential applications such as the development of bio-inspired homogeneous photocatalysts and novel types of metal complex sensitizers for solar cell devices based on abundant and environmentally benign materials.

¹ The deviation from the linearity for some solvents might stem from a coordination of solvent molecules or from some dissociation in different solvent.

Table 3					
Crystal data.	data collection	and structure	refinement f	for compounds	1 - 3

	1	2	3
Formula	C ₇₂ H ₈₀ Cl ₂ Cu ₂ N ₄	$C_{72}H_{80}Br_2Cu_2N_4$	C72H80I2Cu2N4
$M_{\rm W}$ (g/mol)	1199.40	1288.30	1382.30
Crystal size (mm)	$0.34 \times 0.22 \times 0.20$	$0.29 \times 0.28 \times 0.22$	$0.34 \times 0.18 \times 0.14$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	16.4186(12)	16.493(2)	15.1455(2)
b (Å)	12.4409(10)	12.415(2)	13.44971(17)
<i>c</i> (Å)	16.4453(11)	16.528(2)	16.2721(2)
α (°)	90.00	90.00	90.00
β (°)	93.388(8)	91.616(15)	91.3972(12)
γ (°)	90.00	90.00	90.00
$V(Å^3)$	3353.3(4)	3382.9(8)	3313.68(7)
$ ho_{ m ber}~(m mg~cm^{-3})$	1.112	1.257	1.316
Z	2	2	2
$\mu (\mathrm{mm}^{-1})$	1.188	1.265	1.385
T (K)	296(1)	297(1)	123
Θ range (°)	2.05-25.84	2.05-25.88	4.04-66.81
λ (Å)			
Reflections collected	24 175	30 789	13 559
Unique reflections	$6416 [R_{int} = 0.0563]$	$6219 [R_{int} = 0.0861]$	5672 [R _{int} = 0.0331]
Observed reflections $[I > 2\sigma(I)]$	3081	2910	4582
Data/restraints/parameters	6416/0/361	6219/0/369	5672/0/361
Absorption correction	analytical	analytical	semi-empirical
T_{\min}, T_{\max}	0.9171, 0.7729	0.8049, 0.5689	1.00000, 0.46513
$\sigma_{\rm fin}$ (maximum/minimum) (e Å ⁻³)	0.289/-0.209	0.670/-0.402	0.795/-0.619
$R_1 \ [I \geqslant 2\sigma(I)]$	0.0355	0.0355	0.0336
wR ₂	0.0773	0.0937	0.0865
CCDC	810735	810736	810737

3. Experimental section

3.1. General methods

All chemicals were purchased in reagent grade quality and directly used as received. Unless otherwise stated, commercially available organic solvents of standard quality were purified and dried according to the accepted general procedures. Elemental analyses were performed at the Centre for Chemical Analysis of the Faculty of Natural Sciences of the University of Regensburg. Electronic absorption spectra were recorded with a Cary 300 Bio UV-Vis spectrophotometer using 1 cm quartz cells. NMR spectra were recorded with a Bruker Digital Avance NMR-spectrometer DPX200 (¹H: 200.1 MHz; ¹³C: 50.3 MHz; *T* = 303 K). The chemical shifts are reported in ppm relative to external standards (solvent residual peak), and coupling constants are given in Hertz. The spectra were analyzed as being first order. Error of reported values: 0.01 ppm for ¹H NMR and 0.1 Hz for coupling constants. The solvent used is reported for each spectrum. Mass spectra were recorded with a LCQ DECA XP Plus (ESI). Infrared spectra were recorded with a FT-IR-Spectrometer Paragon PC.

3.2. Synthesis

The preparation of all compounds described in the present work was carried out according to the following general procedure: CuX (X = Cl, Br and I) and the Pr_2 -Ph-BIAN ligand were stirred in 20 ml of dichloromethane at room temperature for 12 h. Approximately 10 ml pentane were added to fully precipitate the complex. The product was washed with pentane and re-crystallized from DCM/ pentane.

3.3. [(Pr₂-Ph-BIAN)CuCl]₂ (1)

Reaction of CuCl (50 mg, 0.50 mmol) and Pr₂–Ph–BIAN (250 mg, 0.50 mmol) yielded 237 mg (79%) of a violet powder. ¹H NMR (200 MHz, CDCl₃) δ = 8.06 (d, ³*J*_{HH} = 10.50 Hz, 4H), 7.27–7.51 (m, Ar), 6.80 (m, 4H), 3.08 (m, Isopropyl, 4H), 1.56–1.01 (m, Me, 48H)

ppm. MS (ESI): m/z 1198.00 [M]⁺, 1161.07 [M–Cl]⁺. Anal. Calc. for C₇₂H₈₀Cl₂Cu₂N₄ (1199.40): C, 72.10; H, 6.72; N, 4.67. Found: C, 71.88; H, 6.39; N, 4.56%. UV–Vis (CH₂Cl₂): λ (log ε) = 259 sh (69 000), 270 sh (51 800), 311 sh (24 600), 326 (27 800), 341 sh (27 800), 408 (13 600) nm. IR (KBr) ν = 2958 (m, –C–H), 1643 (s, C=N–), 1281 (s, C–N) cm⁻¹.

3.4. [(Pr₂-Ph-BIAN)CuBr]₂ (**2**)

Reaction of CuBr (50 mg, 0.35 mmol) and Pr₂–Ph–BIAN (174 mg, 0.35 mmol) yielded 162 mg (72%) of a violet powder. ¹H NMR (200 MHz, CDCl₃) δ = 1.25–1.54 (br), 8.24 (br) ppm. MS (ESI): *m/z* 1163.20 [M–Br]⁺. *Anal.* Calc. for C₇₂H₈₀N₄Cu₂Br₂ (1288.30): C, 67.12; H, 6.26; N, 4.35. Found: C, 67.14; H, 6.00; N, 4.31%. UV–Vis (CH₂Cl₂): λ (log ε) = 257 *sh* (38 100), 271 (26 700), 307 *sh* (13 000), 326 (15 000), 340 *sh* (12 400), 424 (6800) nm. IR (KBr) ν = 2958 (m, –C–H), 1645 (s, C=N–), 1281 (s, C–N) cm⁻¹.

3.5. [(Pr₂-Ph-BIAN)Cul]₂ (3)

Reaction of Cul (50 mg , 0.26 mmol) and Pr₂–Ph–BIAN (131 mg, 0.26 mmol) yielded 130 mg (72%) of a violet powder. ¹H NMR (300 MHz, CDCl₃) δ = 8.04 (d, ³*J*_{HH} = 8.45 Hz, 4H), 7.24–7.48 (m, Ar), 6.79 (m, 4H), 3.08 (m, Me₂C–H, 4H), 0.99–1.54 (m, Me, 48H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 22.59 (+, 2C), 22.96 (s, 2C), 28.10 (s, 2C), 122.93 (s), 127.38 (s, 2C), 128.38 (s), 128.99 (s, 2C), 130.31 (s), 134.92 (s, 2C), 147.01 (s, 2C), 160.47 (s), 166.13 (s, 2C) ppm. MS (ESI): *m/z* 1255.00 [M–I]⁺. *Anal.* Calc. for C₇₂H₈₀N₄Cu₂I₂ (1382.30): C, 62.56; H, 5.83; N, 4.05. Found: C, 62.73; H, 5.70; N, 3.98%. UV–Vis (CH₂Cl₂): λ (log ε) = 259 *sh* (59 400), 274 (38 800), 318 *sh* (28 500), 323 (28 500), 341 *sh* (22 200), 434 (12 600) nm. IR (KBr) ν = 2958 (m, –C–H), 1645 (s, C=N–), 1282 (s, C–N) cm⁻¹.

3.6. Crystal structures

Diffraction data for crystals of the compounds **1–3** were collected with a STOE-IPDS diffractometer [30] with graphite-mono-

chromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SIR-97) [31] and refined by full-matrix least-squares an F^2 (SHELXL-97) [32]. The H atoms were calculated geometrically and a riding model was applied during the refinement process. Further crystallographic refinement data can be found in Table 3.

Acknowledgments

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Appendix A. Supplementary material

CCDC 810735, 810736, 810737 contain the supplementary crystallographic data for **1**, 2 and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.042.

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