Copper(I) Complexes with a Proximal Aromatic Ring: Novel Copper–Indole Bonding**

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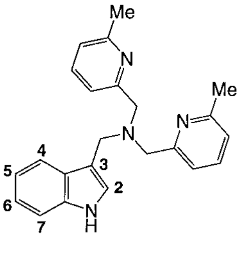
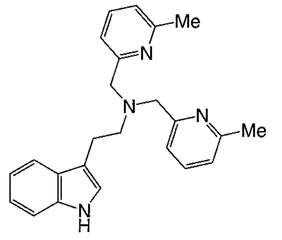
Noncovalent interactions between metal ions and aromatic rings have been implicated for copper(II) complexes such as [Cu(bpy)(L-Trp)(H_2O)]ClO_4[1] and [Cu(phen)(L-Trp)]ClO_4[2] (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Trp = tryptophanate), where stacking between the side chain and coordinated aromatic rings, and close contact between the metal ion and the aromatic ring have been detected. Even in the absence of a coordinated aromatic ring as a stacking partner, the indole ring in Cu^{II} – glycyltryptophanate[3] and the phenol ring in [Cu(L-Tyr)$_2$][4] (Tyr = tyrosinate) have been found to be close to the Cu^{II} ion with a square-planar geometry, which indicated that there could be a bonding interaction between the Cu^{II} ion and the aromatic ring. Recently a Cu^I – macrocyclic NS_2 ligand complex with a naphthyl ring was structurally characterized to have a bond between the Cu^I center and the naphthyl ring π bond.[5] Our preliminary ab initio molecular orbital calculations with the density functional method supported the formation of a bonding orbital between the Cu^{II} ion and the five-membered ring of the indole nucleus above the coordination plane in [Cu(bpy)(L-Trp)(H_2O)]$^+$.[6] Herein we report that a tridentate N-donor ligand with a pendent indole group forms a distorted tetrahedral Cu^I complex that involves a unique coordination of the indole ring through the indole C(2)–C(3) moiety.

A tridentate ligand, *N*-(3-indolylmethyl)-*N*,*N*-bis(6-methyl-2-pyridylmethyl)amine (Me_2IMP) or *N*-(3-indolylethyl)-*N*,*N*-bis(6-methyl-2-pyridylmethyl)amine (Me_2IEP), was treated with [Cu(CH_3CN)$_4$]PF_6 in methanol to give crystals of [Cu(Me_2IMP)(CH_3CN)]PF_6 (**1**) and [Cu(Me_2IEP)]PF_6 (**2**), respectively. X-ray crystal structure analyses[7] have shown that they have structures with different conformations of the aromatic side chain, which depend on the length of the 3-indolylalkyl chain. The unit cell of **1** consists of two crystallographically independent Cu^I complex ions and two PF_6^- ions. The molecular structure is shown in Figure 1, where the coordination around the Cu^I ion has a tetrahedral geometry formed by two pyridine nitrogen atoms, a tertiary amine nitrogen atom, and an acetonitrile nitrogen atom. The side-chain indole ring is uncoordinated, and no stacking or Cu – aromatic ring interaction was detected. Complex **2** has the structure shown in Figure 2, with the Cu^I ion bound in a distorted tetrahedral geometry to three nitrogen atoms and the C(2)–C(3) moiety of the indole ring. The C(2)–C(3) bond length in **2** (1.379(7) Å) is only slightly longer than that of the uncoordinated indole ring in **1** (1.365(9) Å), which is in line with the observation that the C–C bond length of coordinated ethylene (1.329 – 1.360 Å) in several Cu^I – alkene complexes[8] is virtually unchanged from that of free ethylene (1.337 Å).[9] Whereas the Cu^I – naphthyl bond in the Cu^I complex of the macrocyclic ligand has one short (2.129(6) Å) and one long (2.414(6) Å) Cu–C bond,[5] the two Cu–C bond lengths in **2** (2.228(5) and 2.270(5) Å for Cu–C(2) and Cu–C(3), respectively) are nearly the same, but the two bonds are much longer than those in Cu^I – ethylene complexes (1.943 – 2.028 Å).[8] We see from the structures of **1** and **2** and the space-filling models



Me_2IMP



Me_2IEP

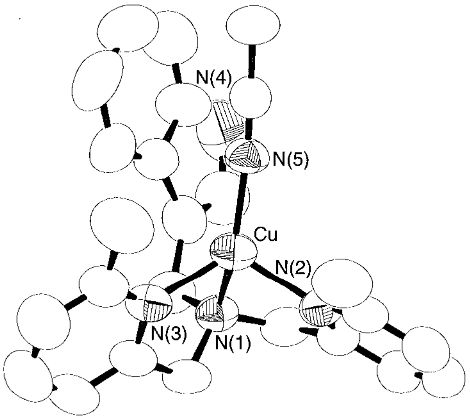


Figure 1. ORTEP view of the [Cu(Me_2IMP)(CH_3CN)]$^+$ ion in **1** drawn with the thermal ellipsoids at the 50 % probability level and atomic labeling scheme.

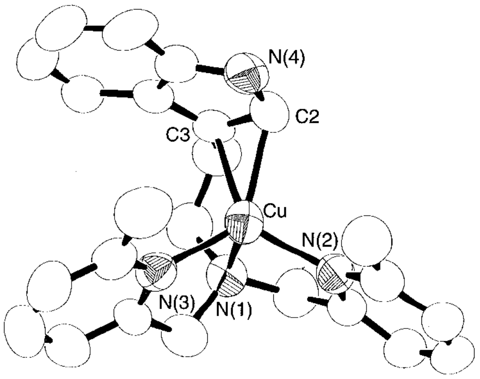


Figure 2. ORTEP view of the [Cu(Me_2IEP)]$^+$ ion in **2** drawn with the thermal ellipsoids at the 50 % probability level and atomic labeling scheme.

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that the observed structural difference may be a consequence of the steric requirements for the side-chain indole ring to approach the Cu^I center. In connection to this, a closely related tripodal ligand, tris(6-phenyl-2-pyridylmethyl)amine, with an additional substituted pyridine ring in place of an indole ring of Me$_2$IEP is reported to form a Cu^I complex with a trigonal pyramidal geometry with four nitrogen atoms coordinated.[10]

The absorption spectrum of **2** in CH_2Cl_2 exhibited a characteristic band centered at 308 nm ($\varepsilon = 18000$), which is assigned to the charge transfer from Cu^I to the indole ring (metal to ligand charge transfer (MLCT)). This band disappeared when **2** was dissolved in CH_3CN, and the resulting spectrum was similar to that of **1**, which has no Cu^I–indole bonding. This indicates that the indole ring in **2** is weakly bound to Cu^I and is easily replaced by CH_3CN. The ^{1}H NMR chemical shift differences between the indole protons of the complexes and those of the free ligands were found to be rather small, which is in contrast with the finding that Cu^I-coordinated styrene exhibits upfield shifts of $\Delta\delta = 0.1-0.5$ as a result of the π back donation.[11] On the other hand, whereas the spectrum of Me$_2$IEP in CD_2Cl_2 showed the ethylene signals at $\delta = 2.96$ as a multiplet, two separate triplets were observed for **2** at $\delta = 3.03$ and 3.25, which demonstrates that the two methylene groups ($-CH_2CH_2-$) are not equivalent as a result of the coordination of the indole ring.

The cyclic voltammograms of **1** and **2** were recorded in CH_2Cl_2 under a nitrogen atmosphere to give quasi-reversible redox waves with $E_{1/2} = -0.06$ V ($\Delta E = 0.12$ V) and 0.01 V ($\Delta E = 0.15$ V) versus ferrocene/ferrocenium, respectively. The finding that **2** has a higher redox potential than that of **1** may be interpreted as a result of the π back donation from the Cu^I ion to the coordinated indole ring.

In conclusion, the Cu^I complexes of two indole-containing ligands have different structures that depend either on the side-chain length or the mobility of the indole ring. Despite the various types of direct metal–indole bonds that have been reported,[12–15] complex **2** presents a novel mode of metal binding by the indole ring and suggests the reactivity of the C(2)–C(3) moiety and the versatility of the indole ring are important in metal complex formation.

Experimental Section

Me$_2$IMP: Indole (1.77 g, 10 mmol) and a small amount of acetic acid was added to a solution of bis(6-methyl-2-pyridylmethyl)amine (2.27 g, 10 mmol) in methanol (100 mL). Aqueous formaldehyde (37%, 0.81 g) was added in small portions to the resulting solution with stirring. The reaction mixture was stirred for two days at room temperature and then concentrated almost to dryness under a reduced pressure. The residue was dissolved in a saturated aqueous solution of $NaHCO_3$ (50 mL) and extracted with $CHCl_3$ (3×50 mL). The brown oily product obtained from the extract was purified by column chromatography on silica gel with $CHCl_3$/methanol as eluent to give Me$_2$IMP (2.01 g, 56.3%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 2.51$ (s, 6H, CH_3py), 3.81 (s, 4H, CH_2py), 3.87 (s, 2H, CH_2indole), 6.98 (d, 2H, py-H), 7.10–7.16 (m, 2H, indole-4,7-H), 7.20 (d, 1H, indole-2-H), 7.33 (m, 1H, indole-5,6-H), 7.43 (d, 2H, py-H), 7.53 (t, 2H, py-H), 7.71 (m, 1H, indole-5,6-H), 8.1 (brs, 1H, indole-NH).

Me$_2$IEP: Tryptamine (2.70 g, 16.8 mmol) and a small amount acetic acid was added to a solution of 6-methylpyridine-2-aldehyde (4.08 g, 33.7 mmol) in methanol (100 mL). Sodium cyanotrihydroborate (2.14 g, 33.7 mmol) was added in small portions to the resulting solution with stirring. The reaction mixture was stirred for three days at room temperature, acidified with conc. HCl, and then concentrated almost to dryness under a reduced pressure. The residue was dissolved in a saturated aqueous solution of $NaHCO_3$ (50 mL) and extracted with $CHCl_3$ (3×50 mL). The brown oily product obtained from the extract was purified by column chromatography on silica gel with $CHCl_3$/methanol as eluent to give Me$_2$IEP (4.34 g, 70.2%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 2.53$ (s, 6H, CH_3py), 2.96 (m, 4H, CH_2CH_2), 3.92 (s, 4H, CH_2py), 6.94 (d, 1H, indole-2-H), 6.98 (d, 2H, py-H), 7.03–7.15 (m, 2H, indole-4,7-H), 7.32 (d, 2H, py-H), 7.32 (m, 1H, indole-5,6-H), 7.44 (m, 1H, indole-5,6-H), 7.46 (t, 2H, py-H), 8.0 (brs, 1H, indole-NH).

1 and **2**: The complexes were prepared in methanol under a nitrogen atmosphere from $[Cu(CH_3CN)_4]PF_6$ and Me$_2$IMP and Me$_2$IEP, respectively, as pale yellow crystals. **1**: Yield, 59%; ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): $\delta = 2.69$ (s, 6H, CH_3py), 3.68 (d, 2H, CH_2py), 4.06 (s, 2H, CH_2indole), 4.08 (d, 2H, CH_2py), 7.06 (d, 2H, py-3,5-H), 7.07 (dd, 1H, indole-5,6-H), 7.13 (td, 1H, indole-5,6-H), 7.22 (d, 2H, py-3,5-H), 7.36 (d, 1H, indole-2-H), 7.39 (m, 1H, indole-4,7-H), 7.42 (dt, 1H, indole-4,7-H), 7.63 (t, 2H, py-4-H), 9.36 (brs, 1H, indole-1-H); elemental analysis (%) calcd for $C_{25}H_{27}N_5CuF_6P$: C 49.54, H 4.49, N 11.55; found: C 49.41, H 4.60, N 11.24. **2**: Yield, 64%; ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): $\delta = 2.64$ (s, 6H, CH_3py), 3.03 (t, 2H, CH_2CH_2), 3.25 (t, 2H, CH_2CH_2), 3.80 (d, 2H, CH_2py), 4.10 (d, 2H, CH_2py), 6.98 (td, 1H, indole-5,6-H), 7.10 (d, 1H, indole-2-H), 7.16 (m, 1H, indole-5,6-H), 7.16 (m, 2H, py-3,5-H), 7.24 (d, 2H, py-3,5-H), 7.31 (d, 1H, indole-4,7-H), 7.44 (d, 1H, indole-5,8-H), 7.69 (t, 2H, py-4-H), 8.96 (brs, 1H, indole-1-H); elemental analysis (%) calcd for $C_{24}H_{26}N_4CuF_6P$: C 49.78, H 4.53, N 9.68; found: C 50.08, H 4.50; N 9.65.

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[7] X-Ray crystal structure determination: The X-ray diffraction data were collected at 295 K with a Rigaku AFC-5R four-circle diffractometer and graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Crystal data for **1**: $C_{25}H_{27}N_5CuF_6P$, $M_r = 606.03$, crystal size: $0.6 \times 0.3 \times 0.2$ mm, triclinic, space group $P\bar{1}$, $a = 14.109(4)$, $b = 16.601(5)$, $c = 12.392(7)$ Å, $\alpha = 100.86(4)$, $\beta = 90.48(4)$, $\gamma = 90.49(3)°$, $V = 2760(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.458$ g cm^{-3}, $\mu = 22.42$ cm^{-1}, $F(000) = 1240.0$, 9958 independent reflections, 6895 reflections used, 686 parameters, $R = 0.088$, $R_w = 0.088$. Crystal data for **2**: $C_{24}H_{26}N_4CuF_6P$, $M_r = 579.01$, crystal size: $0.6 \times 0.2 \times 0.1$ mm, triclinic, space group $P\bar{1}$, $a = 11.573(1)$, $b = 14.151(1)$, $c = 8.0593(9)$ Å, $\alpha = 104.091(8)$, $\beta = 95.778(8)$, $\gamma = 92.197(8)°$, $V = 1270.9(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.513$ g cm^{-3}, $\mu = 23.93$ cm^{-1}, $F(000) = 592.0$, 3749 independent reflections, 3280 reflections used, 326 parameters, $R = 0.065$, $R_w = 0.066$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-115148 and 115149 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: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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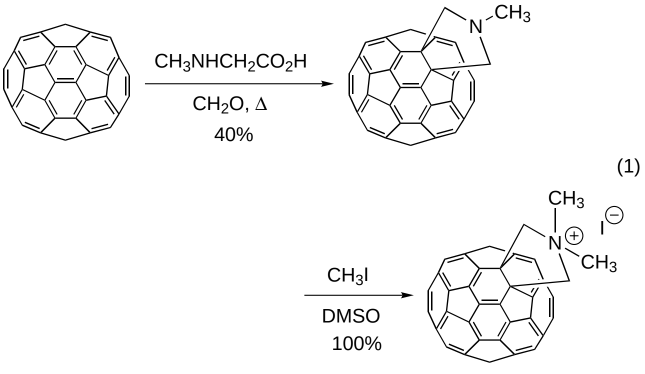
Self-Assembling Supramolecular Nanostructures from a C_{60} Derivative: Nanorods and Vesicles[**]

Alan M. Cassell, C. Lee Asplund, and James M. Tour[*]

Extended fullerene structures such as those found in carbon nanotubes have attracted considerable interest from both structural and applications perspectives.[1] Similarly, nonextended C_{60} derivatives have shown promise for numerous applications.[1] In an effort to bridge the gap between self-assembling, extended structures and modified fullerene materials, we describe here the supramolecular assembly of a derivatized C_{60}. C_{60}-*N*,*N*-dimethylpyrrolidinium iodide (**1**),[2] prepared in two steps from C_{60} [Eq. (1)], can self-assemble into either nanorods or vesicles depending on how the solution is treated.



(1)

1

Nanorod structures were prepared from a two-phase mixture by diluting a solution of **1** in dimethylsulfoxide (DMSO) with one part water and then adding one part benzene (Scheme 1). Two layers were obtained, and the mixture was agitated by shaking until an emulsion formed. The emulsion dissipated after 15 min, and the two layers separated. The benzene layer contained a flocculent, hairlike material (75% yield), which was inspected by transmission electron microscopy (TEM). Rodlike structures were observed with diameters of 14–120 nm and lengths of over 70 μm (Figures 1 a, b). The precise molecular orientation and spacing of **1** in the supramolecular structure is not known; however, that such extended fulleroid structures could self-assemble is striking, especially since a long hydrophobic tail is not appended onto the fullerene rings. To our knowledge, there is no similar process for the rapid supramolecular assembly of fullerenes or their derivatives in such high yields.

The scope of this process was investigated. Self-assembly of **1** into rodlike structures was not seen at concentrations less than 2.5 mM. The precise order of solvent addition was also critical: addition of benzene, then water, to a solution of **1** in DMSO followed by agitation failed to provide nanorods. To screen the effect of different solvents on nanorod formation, benzene was replaced by hexane, cyclohexane, diethyl ether, chloroform, and dichloromethane. The self-assembly experiments in chloroform and dichloromethane were inconclusive, resulting in thick milky white solutions. Using diethyl ether as solvent resulted in two clear layers absent of solid. No self-assembled structures were observed in these layers by TEM. Use of cyclohexane and hexane led to much shorter nanorods having lengths of 1–2 μm and diameters similar to those obtained with benzene.

We also explored changes to **1** that might affect assembly into nanorods. Changing the counterion in a surfactant can influence essential parameters necessary to form micellar structures.[3] In the case of **1**, exchanging the iodide for bromide, chloride, and nitrate did influence the formation of nanorods. Ion exchange of the iodide on **1** was performed by passing a solution of **1** in DMSO through an ion-exchange resin containing the desired anion. Anion exchange was detected by energy dispersive X-ray analysis (EDAX). In the case of nitrate, the absence of iodide by EDAX was proof of counterion exchange since the lighter elements cannot be detected with the system utilized. Under the same conditions employed with the iodide salt, nanorods formed from both the bromide and nitrate salts. However, no rods were detected when chloride was the counterion. We speculate that with the

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