Synthesis of copper(I) complexes with a novel naphthyl-appended macrocyclic ligand, including the crystal and molecular structure of the first copper(I)–η^2-naphthyl complex

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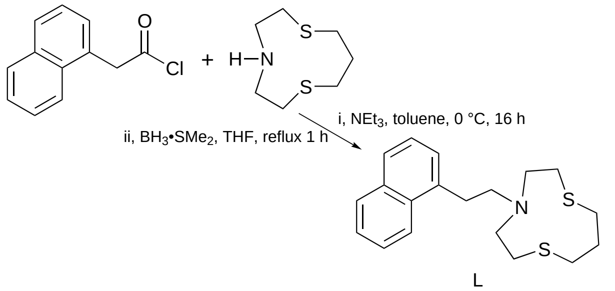
A new ligand, *N*-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane (L), and two of its copper(I) complexes [CuL(MeCN)]PF_6 and [CuL]PF_6, have been synthesized and characterized, including crystal structures of the two copper complexes.

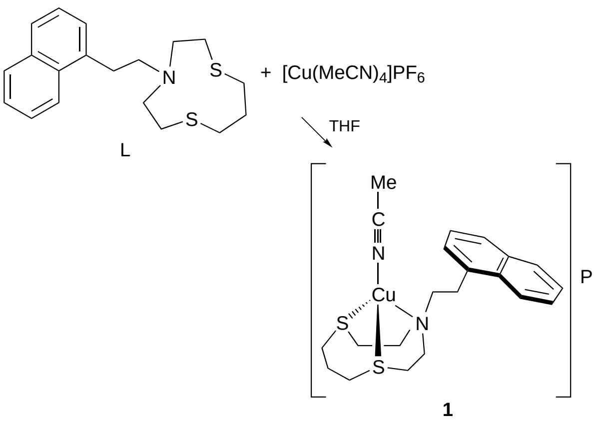
Organocopper compounds are among the most widely used organometallic reagents in the synthetic organic chemist's arsenal, valued for diversity and versatility in effecting transformations.[1] However, knowledge of the structural chemistry for organocopper compounds is as yet underdeveloped.[1a] While a number of σ-bonded alkyl- and aryl-copper(I)[1a,2] as well as copper(I) π-alkene complexes[3] have been structurally characterized, there are only a handful of such reports for copper(I) π-arene and π-aryl complexes. These include a couple of η^5-cyclopentadienyl-ligated copper complexes,[4] and two η^2-benzene complexes, $(C_6H_6)CuAlCl_4$[5] and $(CuOSO_2CF_3)_2C_6H_6$.[6] There are also accounts of weak interactions in the solid state between a Cu^I center and an arene ring, with long distances, typically in the range 2.7–3.0 Å.[7] Here, we report the synthesis and characterization of the first example, to our knowledge, of a structurally characterized copper complex containing a π-bound naphthalene ligand, plus details for a related complex, where an acetonitrile ligand is ligated instead of the naphthyl group, and the synthesis of the naphthyl-appended, macrocyclic-NS_2 ligand.

The novel ligand L, *N*-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane, consists of the NS_2-macrocyclic ligand reported by Chandrasekhar and McAuley[8] to which we have added a pendant naphthalene group. L was synthesized in two steps from the parent macrocycle, Scheme 1. The first step involves formation of a precursor amide by reaction of 8-aza-1,5-dithiacyclodecane with 1-naphthylacetyl chloride (prepared from 1-naphthylacetic acid and PCl_5 by literature methods[9]). The amide was isolated and purified by column chromatography [silica gel, ethyl acetate–hexanes (35 : 65)] and was then, in the second step, reduced to L with borane. The ligand L was isolated as an oil after purification by column chromatography [silica gel, ethyl acetate–hexanes (30 : 70)], in 44% overall yield for the two steps.†

The acetonitrile complex, [CuL(MeCN)]PF_6 **1**, was synthesized by the stoichiometric reaction of $[Cu(MeCN)_4]PF_6$[10] with L in THF at ambient temperature, Scheme 2. Recrystallization from acetonitrile–diethyl ether gave a 61% yield of **1** as yellow crystals. Elemental analysis, as well as ^1H and ^{13}C NMR and IR spectroscopic results are consistent with the formulation for **1**.‡ The solid-state structure (Fig. 1) shows that the geometry about the copper ion is slightly distorted from tetrahedral,§ with unexceptional bond lengths and angles.



Scheme 1



Scheme 2

In order to open a coordination site on the copper center, we wanted to remove the acetonitrile ligand from **1**. We first accomplished this, to synthesize [CuL]PF_6 **2**, by stirring **1** in CH_2Cl_2 under a CO atmosphere, followed by removal of the solvent and CO *in vacuo*. Thus, we were taking synthetic advantage of the tendency many copper(I) complexes have to bind CO weakly and reversibly.[11] However, we found that the CO was not necessary; the acetonitrile ligand from **1** was sufficiently labile that several of cycles of stirring the complex in CH_2Cl_2 followed by removal of the solvent *via* vacuum distillation also yielded **2** in $>$ 85% isolated yield, Scheme 3.¶

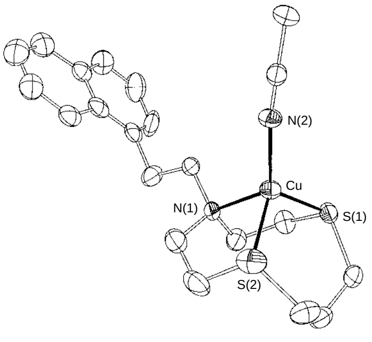
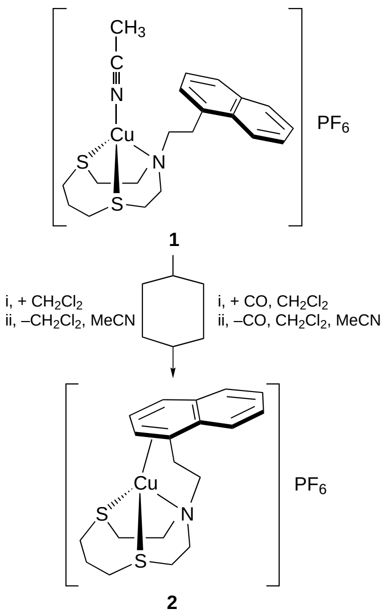


Fig. 1 Thermal ellipsoid plot of the solid-state structure of $[CuL(MeCN)]^+$ at the 25% probability level (hydrogens omitted for clarity). Selected bond distances (Å) and angles (°): Cu–N(1) 2.167(4), Cu–S(1) 2.2687(14), Cu–S(2) 2.260(2), Cu–N(2) 1.923(4); N(1)–Cu–N(2) 118.0(2), S(1)–Cu–N(2) 119.32(14), S(2)–Cu–N(2) 121.73(14), N(1)–Cu–S(1) 90.26(11), N(1)–Cu–S(2) 90.76(12), S(1)–Cu–S(2) 109.04(6).



Scheme 3

Slow diffusion of hexane into a saturated CH_2Cl_2 solution of **2** yielded crystals suitable for X-ray diffraction.§

The solid state structure of **2** (Fig. 2) shows that the copper ion attains a distorted tetrahedral geometry by coordination of the pendant naphthyl group in an η^2-fashion. This binding occurs at the position adjacent to the ethylene linker chain and is unsymmetrical, with the Cu–C(10) and Cu–C(11) distances being 2.414(6) and 2.129(6) Å, respectively [the distance from the Cu to the center of the C(10)–C(11) bond is 2.168 Å]. These distances are comparable to the Cu–C distances in the two known Cu^I–η^2-benzene complexes,[5,6] which range from 2.09 to 2.30 Å. The binding in the previously reported complexes is also unsymmetrical, although it is less pronounced (differences in the pairs of Cu–C distances of 0.03–0.15 Å). Presumably the more accentuated unsymmetrical binding of the η^2-arene in **2** is at least partially due to the relatively short tether chain.

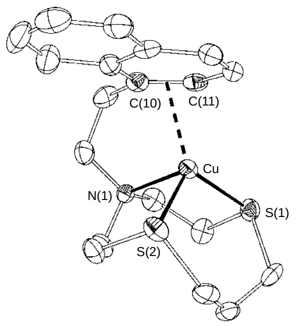


Fig. 2 Thermal ellipsoid plot of the solid-state structure of $[CuL]^+$ at the 25% probability level (hydrogens omitted for clarity). Selected bond distances (Å) and angles (°): Cu–N 2.146(5), Cu–S(1) 2.268(2), Cu–S(2) 2.233(2), Cu–C(10) 2.414(6), Cu–C(11) 2.129(6); N–Cu–S(1) 90.5(2), N–Cu–S(2) 91.89(14), S(1)–Cu–S(2) 111.08(7), N–Cu–C(10) 81.3(2), N–Cu–C(11) 105.4(2), S(1)–Cu–C(10) 133.8(2), S(1)–Cu–C(11) 108.2(2), S(2)–Cu–C(10) 114.5(2), S(2)–Cu–C(11) 136.7(2).

The C(10)–C(11) distance is essentially no longer in **2** [1.384(9) Å] than in **1** [1.343(11) Å]; no discernible differences in the coordinated C–C distances were observed in the two copper–benzene structures either.[5,6] Close comparison of the IR spectra of L and **2** shows that two bands, 1596 and 1509 cm^{-1}, are present in both spectra. In addition, there is a third band that has shifted from 1574 cm^{-1} for L to 1586 cm^{-1} for **2**; we tentatively assign these bands as C=C stretches. The C=C stretches for Cu–alkene complexes have been reported to shift from 15 to 170 cm^{-1} upon coordination.[3*c*,*i*,12]

We are currently exploring the properties of these novel complexes, to offer further insights into the chemistry of this interesting system.

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Notes and References

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† *Selected characterizational data* for L: ^{1}H NMR ($CDCl_3$): δ 8.05 (d, 1 H), 7.86 (dd, 1 H), 7.72 (dd, 1 H), 7.51 (m, 2 H), 7.39 (m, 2 H), 3.30 (m, 2 H), 3.19 (m, 4 H), 2.89 (m, 4 H), 2.87 (m, 2 H), 2.73 (m, 4 H), 1.90 (m, 2 H).

‡ *Selected characterizational data* for **1**: ^{1}H NMR ($CDCl_3$ + 4 equiv. MeCN): δ 7.94 (d, 1 H), 7.88 (d, 1 H), 7.77 (d, 1 H), 7.54 (m, 2 H), 7.42 (m, 1 H), 7.29 (d, 1 H), 3.35 (m, 2 H), 3.21 (m, 4 H), 3.12 (m, 4 H), 3.00 (m, 4 H), 2.77 (m, 2 H), 2.23 (m, 2 H); IR: 2278 mw ν(C≡N).

§ *Crystal data*: **1**: M = 581.08, triclinic, space group $P\bar{1}$ (no. 2), a = 11.1901(10), b = 11.2735(12), c = 12.1350(10) Å, α = 98.996(8), β = 117.188(6), γ = 105.354(7)°, U = 1242.6(2) Å^3, Z = 2, μ(Mo-Kα) = 1.169 mm^{-1}. The structure was solved using Patterson methods and refined on F^2 to R_1 = 0.0505 and R_w = 0.1291 with $I > 2\sigma(I)$, using 3202 unique reflections and 382 parameters. **2**: M = 582.11, monoclinic, space group $P2_1/c$ (no. 14), a = 15.732(2), b = 8.9164(10), c = 17.205(2) Å, β = 102.431(6)°, U = 2356.8(4) Å^3, Z = 4, μ(Mo-Kα) = 1.231 mm^{-1}. The structure was solved using Patterson methods and refined on F^2 to R_1 = 0.0587 and R_w = 0.1285 with $I > 2\sigma(I)$, using 4153 unique reflections and 320 parameters. CCDC 182/742.

¶ *Selected characterizational data* for **2**: ^{1}H NMR ($CDCl_3$): δ 8.00 (d, 1 H), 7.92 (d, 1 H), 7.83 (d, 1 H), 7.63 (m, 2 H), 7.45 (t, 1 H), 7.28 (d, 1 H), 3.40 (br s, 2 H), 3.2–2.4 (br m, 12 H), 2.10 (m, 2 H), 1.46 (m, 2 H).

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