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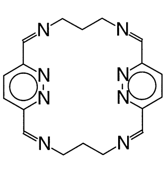
A Grid Complex $[Cu^I_4L_2]^{4+}$ and a Mixed-Valent Complex $[Cu^{II}Cu^IL(MeCN)_2]^{3+}$ of the Pyridazine-Containing Macrocycle L**

Sally Brooker,* Sarah J. Hay, and Paul G. Plieger


L

The Schiff base macrocycle L, obtained from the [2+2] condensation of 3,6-diformylpyridazine[1–4] and 1,3-diaminopropane, has allowed the isolation of a wide range of transition metal complexes with intriguing properties, in particular redox[1,5,6] and magnetic properties.[5–7] To date, many pyridazine-bridged or phthalazine-bridged dicopper(II) complexes,[8–10] but few copper(I) complexes[11–15] and, to our knowledge, no mixed-valent copper complexes, have been isolated. The structure, magnetochemistry, and electrochemistry of the first example of a macrocyclic pyridazine-bridged dicopper complex was reported recently.[5] In contrast to other pyridazine-bridged dicopper complexes, two well-separated one-electron reductions were observed for this dicopper(II) complex, as is seen for related phenolate-bridged complexes,[16] except that, as expected, they occur at more positive potentials due to the π-acceptor properties of L. We report here on the formation and characterization of the mixed-valent complex **1** and the air-stable tetracopper(I) grid complex $[Cu^I_4L_2](PF_6)_4$ (**2**) of the Schiff-base macrocyclic ligand L.

$[Cu^{II}Cu^IL(MeCN)_2](ClO_4)_2(PF_6)$ **1**

The mixed-valent $Cu^{II}Cu^I$ complex **1** is formed by a transmetallation reaction in acetonitrile (see the Experimental Section) and crystallized, in air, in 41 % yield, by diffusion of diethyl ether into the reaction solution. The IR spectrum of **1** shows that the macrocycle is intact. The structure determination of **1**·MeCN (Figure 1) reveals a similar overall structure to that of the dicopper(II) analogue $[Cu^{II}_2L(MeCN)_2]^{4+}$ (**3**).[5] The copper centers are doubly bridged by the pyridazine groups and the macrocycle is fairly flat (the pyridazine ring planes intersect at 23.5(2)°; cf. 29.67(7)° for **3**). In each case four of the nitrogen donors come from the macrocycle (N_{macro}) and the fifth from an acetonitrile solvent molecule. However, the copper ions have distinct geometries consistent with the mixed-valent complex being class I

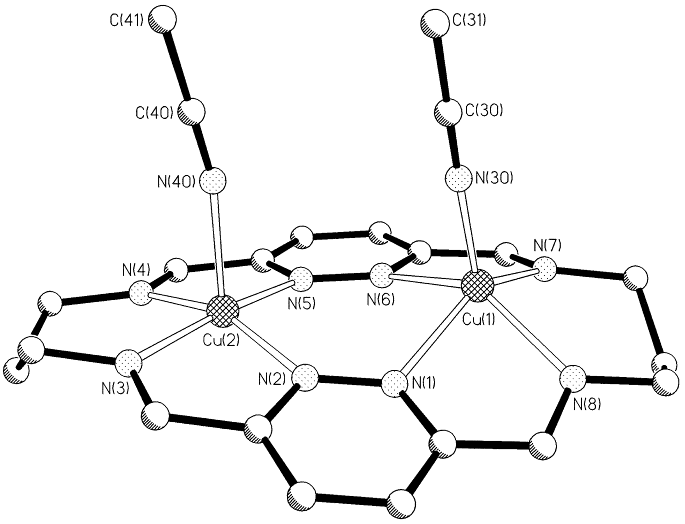


Figure 1. Perspective view of the cation of **1**, $[Cu^{II}Cu^IL(MeCN)_2]^{3+}$. Selected interatomic distances [Å] and angles [°]: Cu(1)-N(30) 1.931(4), Cu(1)-N(7) 2.038(4), Cu(1)-N(8) 2.105(4), Cu(1)-N(1) 2.151(3), Cu(1)-N(6) 2.289(3), Cu(2)-N(3) 1.978(3), Cu(2)-N(5) 2.008(3), Cu(2)-N(4) 2.034(3), Cu(2)-N(2) 2.072(3), Cu(2)-N(40) 2.157(4), Cu(1)···Cu(2) 3.9599(9); N(30)-Cu(1)-N(7) 115.87(15), N(30)-Cu(1)-N(8) 115.62(14), N(7)-Cu(1)-N(8) 91.49(15), N(30)-Cu(1)-N(1) 102.05(14), N(7)-Cu(1)-N(1) 141.48(13), N(8)-Cu(1)-N(1) 77.37(13), N(30)-Cu(1)-N(6) 104.39(13), N(7)-Cu(1)-N(6) 75.18(14), N(8)-Cu(1)-N(6) 139.62(13), N(1)-Cu(1)-N(6) 89.64(12), N(3)-Cu(2)-N(5) 168.97(13), N(3)-Cu(2)-N(4) 92.85(14), N(5)-Cu(2)-N(4) 80.48(13), N(3)-Cu(2)-N(2) 80.42(13), N(5)-Cu(2)-N(2) 102.93(13), N(4)-Cu(2)-N(2) 160.04(13), N(3)-Cu(2)-N(40) 92.51(14), N(5)-Cu(2)-N(40) 97.09(14), N(4)-Cu(2)-N(40) 98.03(15), N(2)-Cu(2)-N(40) 101.00(14), C(30)-N(30)-Cu(1) 178.2(4), C(40)-N(40)-Cu(2) 168.1(4).

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(localized valence) at 173 K in the solid state (consistent with this, a four-line EPR spectrum is observed for **1** as a DMF glass at 133 K). The copper(I) ion, Cu(1), has a distorted five-coordinate geometry and is located 0.723(2) Å out of the plane of the four N_{macro} donors, whereas the copper(II) ion, Cu(2), has a distorted square-pyramidal geometry and is only 0.257(2) Å out of the plane of the four N_{macro} donors (cf. 0.317(2) Å for copper(II) in **3**). As expected, the $Cu^{I}-N_{macro}$ bond lengths are longer (av $Cu(1)-N_{macro}$ 2.146(4) Å) than those observed for $Cu^{II}-N_{macro}$ (av $Cu(2)-N_{macro}$ 2.023(4) Å; cf. 2.006(3) Å in **3**).[8] The $Cu-N_{MeCN}$ bond lengths reveal a Jahn–Teller distortion for the copper(II) ion in **1** ($Cu(2)-N_{MeCN}$ 2.157(4) Å versus $Cu(1)-N_{MeCN}$ 1.931(4) Å), as was observed in **3** ($Cu-N_{MeCN}$ 2.128(3) Å).

In marked contrast to the dicopper mixed-valent product **1** obtained by transmetallation of a lead–macrocycle complex with copper(I), the product upon use of a copper(I) template in the reaction of the macrocycle components, 3,6-diformylpyridazine and 1,3-diaminopropane, is a tetracopper(I) grid complex, $[Cu^{I}_{4}L_{2}](PF_{6})_{4}$ (**2**, 61% yield). An imine stretch is observed in the IR spectrum at 1627 cm^{-1} and there is no evidence of amine or carbonyl absorptions. Crystals of **2**·2MeCN·0.5Et_2O were grown from the acetonitrile reaction solution by diffusion of diethyl ether, and the X-ray structure determination was carried out (Figure 2). A square of four-coordinate copper(I) ions is ligated by two folded (2+2) macrocycles. Each macrocycle provides a bidentate $N_{imine}N_{pyridazine}$ donor set to each copper atom (bite angle 79.7(6)–81.7(6)°). For each copper atom the two bidentate chelate planes ($CuN_{imine}N_{pyridazine}$, one bidentate donor set from each macrocycle) intersect at approximately right angles (79.8–101.4°). The pyridazine rings within each folded macrocycle lie over each other and are almost parallel (the pyridazine rings of N(1) and N(5) form an angle of 0.9(5)° and are separated by 3.58–3.61(2) Å; the pyridazine rings of N(31) and N(35) form an angle of 2.9(6)° and are separated by 3.57–3.72(2) Å). This is very similar to the arrangement of the pyridazine rings in the tetracopper(I) grid of the acyclic 3,6-bis(2′-pyridyl)pyridazine (dppn) ligand of Youinou and co-workers.[15]

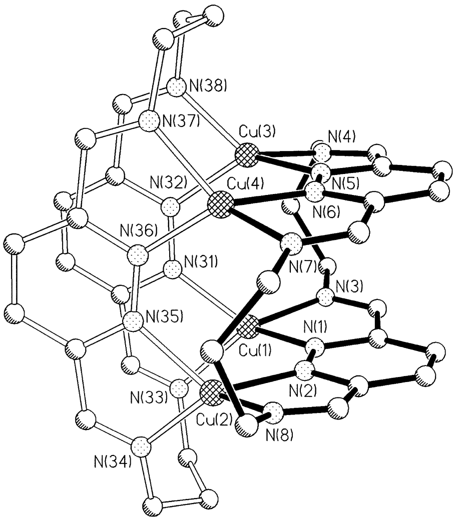

Figure 2. Perspective view of the cation of **2**, $[Cu^{I}_{4}L_{2}]^{4+}$. Selected interatomic distances [Å] and angles [°]: Cu(1)-N(1) 1.973(14), Cu(1)-N(31) 2.016(12), Cu(1)-N(3) 2.032(13), Cu(1)-N(33) 2.040(14), Cu(2)-N(8) 2.001(14), Cu(2)-N(2) 2.001(14), Cu(2)-N(34) 2.049(14), Cu(2)-N(35) 2.067(14), Cu(3)-N(32) 1.994(14), Cu(3)-N(5) 1.991(13), Cu(3)-N(4) 2.014(13), Cu(3)-N(38) 2.037(12), Cu(4)-N(36) 1.956(14), Cu(4)-N(6) 2.022(13), Cu(4)-N(7) 2.059(14), Cu(4)-N(37) 2.050(14), Cu(1)···Cu(2) 3.733(3), Cu(1)···Cu(3) 3.711(3), Cu(1)···Cu(4) 5.228(3), Cu(2)···Cu(3) 5.310(3), Cu(2)···Cu(4) 3.738(3), Cu(3)···Cu(4) 3.726(3); N(1)-Cu(1)-N(31) 128.6(5), N(1)-Cu(1)-N(3) 80.1(6), N(31)-Cu(1)-N(3) 120.0(5), N(1)-Cu(1)-N(33) 121.7(6), N(31)-Cu(1)-N(33) 79.7(6), N(3)-Cu(1)-N(33) 134.1(6), N(8)-Cu(2)-N(2) 81.2(6), N(8)-Cu(2)-N(34) 134.3(5), N(2)-Cu(2)-N(34) 123.7(5), N(8)-Cu(2)-N(35) 118.0(6), N(2)-Cu(2)-N(35) 123.9(6), N(34)-Cu(2)-N(35) 81.7(6), N(32)-Cu(3)-N(5) 130.6(5), N(32)-Cu(3)-N(4) 120.2(5), N(5)-Cu(3)-N(4) 80.3(5), N(32)-Cu(3)-N(38) 81.1(5), N(5)-Cu(3)-N(38) 119.6(5), N(4)-Cu(3)-N(38) 132.6(5), N(36)-Cu(4)-N(6) 129.4(5), N(36)-Cu(4)-N(7) 123.8(6), N(6)-Cu(4)-N(7) 79.9(5), N(36)-Cu(4)-N(37) 80.2(6), N(6)-Cu(4)-N(37) 118.9(5), N(7)-Cu(4)-N(37) 132.0(5).

These findings, along with the results of deliberate syntheses of grids using related pyridazine ligands,[15,17–20] indicate that the way is indeed clear for producing families of grid complexes from ligands related to L.[17] The successful template synthesis of the Schiff base macrocycle L on this tetracopper(I) grid is a significant extension of these studies.

Experimental Section

1: To a refluxing suspension of $[Pb_{2}L'](ClO_{4})_{4}$ (0.199 g, 0.13 mmol; L′ is the (4+4) analogue of the (2+2) macrocycle L)[1] in dry, degassed acetonitrile (40 mL) was added solid $[Cu(CH_{3}CN)_{4}](PF_{6})$[21] (0.197 g, 0.53 mmol). The resulting brown mixture was refluxed under argon for 45 min, during which time the solution clarified. The argon atmosphere was removed, and complex **1** was isolated as a brown crystalline solid by vapor diffusion of diethyl ether into the reaction solution (0.090 g, 41%). Elemental analysis calcd for $C_{18}H_{20}N_{8}Cl_{2}O_{8}PF_{6}Cu_{2}$: C 26.4, H 2.5, N 13.7; found: C 27.0, H 2.7, N 14.0; IR (KBr): $\tilde{\nu} = 1645$, 1101, 839, 623, 558 cm^{-1}; FAB-MS: m/z: 575 $[Cu_{2}L(ClO_{4})]^{+}$, 474 $[Cu_{2}L]^{+}$; molar conductivity (CH_3CN): $\Lambda_{m} =$ 383 mol^{-1} cm^{2} Ω^{-1} (cf. 340–420 mol^{-1} cm^{2} Ω^{-1} for a 3:1 electrolyte in CH_3CN[22]); UV/Vis (CH_3CN): λ_{max} (ε) = 449 (3730), 410 nm sh (3145 L mol^{-1} cm^{-1}).

Crystal data for **1** ($C_{24}H_{29}Cl_{2}Cu_{2}F_{6}N_{11}O_{8}P$): black oblong block, 0.88 × 0.58 × 0.37 mm, monoclinic, space group $P2_{1}/c$, $a = 11.802(2)$, $b = 30.042(6)$, $c = 11.197(2)$ Å, $\beta = 116.262(3)°$, $V = 3560(1)$ Å^3, $Z = 4$, $\mu = 1.48$ mm^{-1}. Of 45348 reflections collected, 7251 were independent and used in the structure analysis. The structure was solved by direct methods (SHELXS-97)[23, 24] and refined against all F^2 data (SHELXL-97)[25] to $R1 = 0.0516$ for 5959 data with $F > 4\sigma(F)$; $wR2 = 0.1405$, GOF = 1.04 for all 7251 data (F^2); 526 parameters. All non-hydrogen atoms were anisotropic, and one perchlorate ion was disordered over two sets of oxygen atom sites.

2: To a yellow solution of 3,6-diformylpyridazine (0.095 g, 0.70 mmol)[1] in dry degassed acetonitrile (20 mL) was added solid $[Cu(CH_{3}CN)_{4}](PF_{6})$[21] (0.261 g, 0.70 mmol) and 1,3-diaminopropane (0.052 g, 0.70 mmol) in dry degassed acetonitrile (10 mL). The resulting brown mixture was stirred under argon for 12 h, and the argon atmosphere removed. On vapor diffusion of diethyl ether into the reaction solution, **2** formed as a brown crystalline solid (0.163 g, 61%). Elemental analysis calcd for $C_{36}H_{40}N_{16}P_{4}F_{24}Cu_{4}$: C 28.3, H 2.6, N 14.6; found: C 28.5, H 2.4, N 14.5; IR (KBr): $\tilde{\nu} = 1627$, 840, 558 cm^{-1}; ^{1}H NMR ($CD_{3}NO_{2}$, referenced to solvent, 298 K): $\delta = 8.94$, 8.35, ca. 4.3 (obscured by solvent), 4.17, 2.05; FAB-MS: m/z: 1385 $[Cu_{4}L_{2}(PF_{6})_{3}]^{+}$, 1240 $[Cu_{4}L_{2}(PF_{6})_{2}]^{+}$, 1095 $[Cu_{4}L_{2}(PF_{6})]^{+}$, 474 $[Cu_{2}L]^{+}$; molar conductivity (CH_3CN): $\Lambda_{m} =$ 550 mol^{-1} cm^{2} Ω^{-1} (cf. 340–420 mol^{-1} cm^{2} Ω^{-1} for a 3:1 electrolyte in CH_3CN[22]); UV/Vis (CH_3CN): λ_{max} (ε) = 410 nm (19170 L mol^{-1} cm^{-1}).

Crystal data for **2**·2MeCN·0.5Et_2O ($C_{42}H_{51}Cu_{4}F_{24}N_{18}O_{0.50}P_{4}$): red-black plate, 0.76 × 0.36 × 0.02 mm, monoclinic, space group Cc, $a = 17.712(7)$, $b = 18.520(7)$, $c = 19.864(7)$ Å, $\beta = 99.004(4)°$, $V = 6436(4)$ Å^3, $Z = 4$, $\mu = 1.52$ mm^{-1}. Of 40404 reflections collected, 10707 were independent and used in the structure analysis. The structure was solved by direct methods (SHELXS-97)[23, 24] and refined against all F^2 data (SHELXL-97)[25] to

$R1 = 0.0945$ for 4546 data with $F > 4\sigma(F)$; $wR2 = 0.2583$, GOF = 0.96 for all 10707 data (F^2); 571 parameters; Flack $x = 0.07(3)$. All copper, acetonitrile, and PF_6^- atoms were anisotropic except the fluorine atoms on the disordered PF_6^- ion.

X-ray data were collected at 168 K for **1** and 173 K for **2** on a Bruker SMART diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Reflections were collected in the range $4 < 2\theta < 53°$, and a semiempirical absorption correction was applied. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137503 and -137504. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Intermolecular Trapping of the Nazarov Intermediate: Domino Electrocyclization/[3+2] Cycloadditions with Allylsilanes**

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Reactions that entail the stereoselective creation of multiple carbon–carbon bonds are highly valued for their synthetic utility.[1] In particular, one-step processes that convert readily available, acyclic components into fused or bridged polycyclic products offer a powerful method for increasing molecular complexity.[2] We have described several examples of the deliberate intramolecular trapping of oxyallyl cations generated during the Nazarov cyclization[3] of 1,4-dien-3-ones, which has resulted in the high yield and stereoselective formation of diverse polycyclic products.[4] These studies were predicated on the idea that a pendant alkene trap could intercept the oxyallyl cation intermediate at a rate competitive with the normal elimination pathway, a process that we have termed the "interupted Nazarov" reaction. More surprising was our observation of the high-yield intermolecular trapping of the Nazarov intermediate using silyl hydride.[5] This occurrence suggests a much broader potential for this process.

These results prompted us to investigate the use of simple allylic silanes in the intermolecular trapping of Nazarov intermediates.[6] The well-precedented nucleophilic reactivity of allylsilanes[7] and their relative stability under Lewis acidic conditions suggested that they might function as effective traps of the oxyallyl cation intermediate. The expected 2-allylcyclopentanones could serve as useful building blocks in the construction of a variety of cyclopentanoid targets. Surprisingly, simple allylation was found to be a minor pathway—the major products in most cases were unprecedented bicyclo[2.2.1]heptanones resulting from a formal [3+2] addition of the oxyallyl cation and the alkene.[8, 9] Described below are the preliminary results of this study, which offers a novel, one-step preparation of bridged bicyclic systems from two simple, unsaturated fragments.

Initial experiments employed dienone **1a**[10a,b] and allyltrimethylsilane (**2a**). Treatment of a mixture of these two compounds with $BF_3 \cdot OEt_2$ at low temperature resulted in the formation of several diastereomeric allylated cyclopentanones (**3a–c**) in a combined yield of 43 %, along with 49 % of an entirely different product (as a single isomer) lacking any unsaturation (Scheme 1). The presence of a trimethylsilyl group suggested that this product was either bicyclo[2.2.1]heptanone **4a** or the isomeric bicyclo[3.2.1]octanone **5**, which result from either direct ring closure of the intermediate

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