Copper Complexes

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Dispersion-Force-Assisted Disproportionation: A Stable Two-Coordinate Copper(II) Complex

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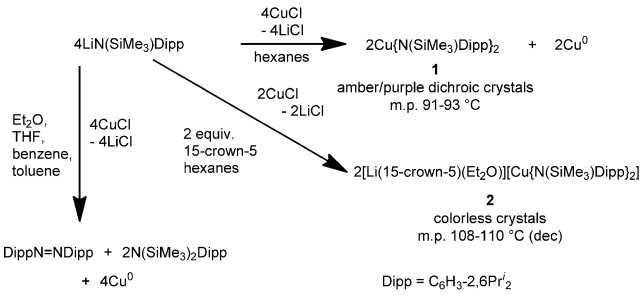
Abstract: *The synthesis of the first linear coordinated Cu^{II} complex $Cu\{N(SiMe_3)Dipp\}_2$ (**1** $Dipp = C_6H_5$-2,6-Pr^i_2) and its Cu^I counterpart $[Cu\{N(SiMe_3)Dipp\}_2]^-$ (**2**) is described. The formation of **1** proceeds through a dispersion force-driven disproportionation, and is the reaction product of a Cu^I halide and $LiN(SiMe_3)Dipp$ in a non-donor solvent. The synthesis of **2** is accomplished by preventing the disproportionation into **1** by using the complexing agent 15-crown-5. EPR spectroscopy of **1** provides the first detailed study of a two-coordinate transition-metal complex indicating strong covalency in the Cu–N bonds.*

There has been much recent interest in the chemical, physical, and magnetic properties of stable open-shell d^1–d^9 two-coordinate transition-metal complexes, mainly because of their possible single-molecule magnetism.[1] The first stable examples, the d^5 Mn^{II} alkyls $Mn\{C(SiMe_3)_3\}_2$[2] and $Mn(CH_2Bu^t)_2$, were reported in 1985,[3] and about 140 complexes, from the first-row Group 5–10 metals, stabilized by a variety of alkyl,[2–4] amido,[5] aryloxo,[6] thiolato,[7] or aryl[8] ligands are now known. However, no open-shell Group 11 examples exist, and the lack of a two-coordinate d^9 Cu^{II} complex is particularly noteworthy, although few three-coordinate Cu^{II} complexes stabilized by large β-diketiminate ligands relevant to the active site in type 1 copper proteins[9a,b] or as catalysts for C–H amination[9c] are known. A difficulty in synthesizing low coordinate Cu^{II} complexes arises from the widely used salt metathesis route in which an alkali metal salt of a ligand is reacted with a Cu^{II} halide. This generally yields reduction of Cu^{II} to Cu^I or Cu^0. We now show that this can be avoided by a metathesis/disproportionation reaction of a Cu^I halide with $LiN(SiMe_3)Dipp$ {$Dipp = C_6H_5$-2,6-Pr^i_2}, a ligand earlier calculated to promote the stabilizing effects of attractive van der Waals forces.[1f,10]

London dispersion forces (LDF), a form of the attractive van der Waals forces between hydrocarbon groups, have been acknowledged as a stabilizing force in many protein structures.[11] Recently, there has been an increasing awareness of their effects in molecular species,[12] particularly those having sterically demanding substituents with numerous C–H···H–C interactions. In most instances, however, the LDF contribution has not been evaluated or recognized.[13] We had calculated that the ligand $^-N(SiMe_3)Dipp$ generates attractive dispersion forces of 21.1–29.4 kcal mol^{-1} in its two coordinate complexes of Fe, Co, and Ni,[1f] and reasoned that a similar degree of stabilization might render isolable the first two-coordinate Cu^{II} species. We now report the characterization of $Cu\{N(SiMe_3)Dipp\}_2$ (**1**) and the related Cu^I salt $[Li(15\text{-crown-}5)Et_2O][Cu\{N(SiMe_3)Dipp\}_2]$ (**2**).

The complex **1** was synthesized by a reaction of a 1:1 ratio of CuCl with $LiN(SiMe_3)Dipp$ (see the Supporting Information). Complex **2** was synthesized from the same reactants in a 2:1 ratio in the presence of 15-crown-5, which favors crystal formation and hinders disproportionation (Scheme 1). The



Scheme 1. Synthesis of **1** and **2**.

mechanism whereby $Cu\{N(SiMe_3)Dipp\}_2$ is obtained from a Cu^I halide precursor is unknown. Possibly, a Cu^I cuprate salt is produced first which then reacts with another equivalent of CuCl eliminating LiCl and Cu metal. In principle, the reaction could also proceed through a neutral Cu^I species $[Cu\{N(SiMe_3)Dipp\}]_n$.[14]

Attempts to obtain copper(II) amides from $CuCl_2$ and alkali metal amido salts have proven unsuccessful in this and other laboratories.[15] Crystals of **1** are stable at room temperature, but when redissolved in unreactive solvents (hexanes, pentane, cyclohexane) they decompose within hours. When the synthesis of **1** from CuCl is attempted in donor (Et_2O, THF, or Me_2S) or aromatic solvents (toluene or benzene), decomposition ensues to yield DippN=NDipp,[1e] $N(SiMe_3)_2Dipp$,[16] and Cu metal.

The X-ray crystal structure[17] of $Cu\{N(SiMe_3)Dipp\}_2$ (**1**; Figure 1) reveals a Cu atom located at an inversion center with rigorously linear geometry and an extended planar

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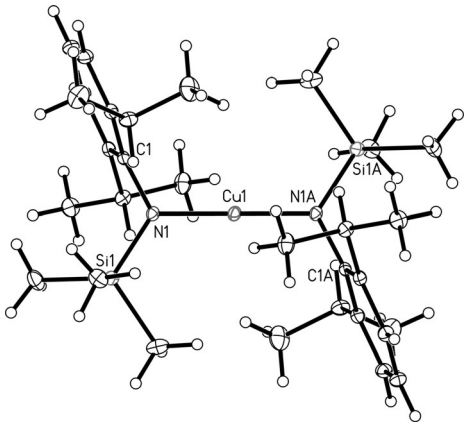


Figure 1. Drawing of **1** with ellipsoids for non-H atoms set at 30% probability. Selected distances [Å] and angles [°]: Cu1–N1 1.7914(10), N1–Si1 1.7574(10), N1–C1 1.4348(14); N1-Cu1-N1A 180, Si1-N1-C1 122.54(8), Si1-N1-Cu1 122.87(6), C1-N1-Cu1 114.52(8).

C(*ipso*)–Si1–N1–Cu1–N1A–Si1A–C(*ipso*) core array. The eclipsed conformation, which maximizes the LDF attractive force,[1f] is also found for its Mg,[18] Mn,[1j] Fe,[1f] Co,[1f] Ni,[1f,19] and Zn[20] analogues. The Cu–N bond length of 1.7914(10) Å is slightly shorter than that in its Ni^{II} congener (1.8029(9) Å).[1e,f,19] The resemblance of the Cu–N and Ni–N distances is consistent with theoretical data for the two-coordinate halides $NiCl_2$ and $CuCl_2$.[21] The Cu–N bond in **1** is ca. 0.05 Å shorter than the Cu–N (amide) distances, ca 1.84 Å, in the three coordinate β-diketiminate Cu^{II} amides.[9a,c]

The Cu^{I} analogue of **1**, the anion $[Cu\{N(SiMe_3)Dipp\}_2]^-$, was crystallized as its 15-crown-5/Et_2O lithium salt $[Li(15\text{-crown-5})Et_2O][Cu\{N(SiMe_3)Dipp\}_2]$ (**2**; Figure 2). It has an average Cu–N distance of 1.869(2) Å, which is longer than the 1.7914(10) Å in **1** owing to the lower metal oxidation state, the negative charge, and higher occupancy of Cu–N π* orbital (see Figure 3B). The Cu coordination is slightly bent at 175.24(10)° and the ligands have a torsion angle of 64.69(6)° similar that of the minima predicted by DFT calculations (see the Supporting Information).

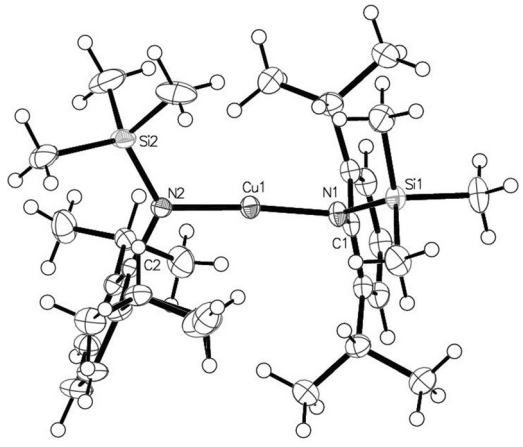


Figure 2. Structure for the anion of **2**. Ellipsoids for non-H atoms are set at 30% probability. Selected distances [Å] and angles [°]: Cu1–N1 1.868(2), Cu1–N2 1.869(3), Si1–N1 1.693(2), Si2–N2 1.693(3), N1–C1 1.413(3), N2–C2 1.422(3); N1-Cu1-N2 175.24(9), C1-N1-Si1 124.02(17), C2-N2-Si2 125.5(2), Si1-N1-Cu1 120.58(11), Si2-N2-Cu1 120.48(16), C1-N1-Cu1 114.77(15), C2-N2-Cu1 113.65(18).

LDF stabilization has been implicated in the structures of several organometallic compounds.[1f,12a,g,22] Its effects have been manifested in bond length contractions,[1f] distorted coordination geometry,[22a] ligand conformation,[12a] and the stabilization of weak bonds between main-group elements.[12a,g] However, the synthesis of **1** demonstrates that dispersion forces can also facilitate disproportionation and stabilize an otherwise unknown coordination number/oxidation state combination. The LDF in **1** was analyzed by reoptimizing (see the Supporting Information) the geometries at the B3PW91-D3 level to yield an M–N bond length of 1.799 Å, in good agreement with the experimental value (1.7914(10) Å). This corresponds to a stabilization energy of 20.8 kcal mol^{-1}.

Magnetic susceptibility measurements on **1** by SQUID magnetometry yield a maximum magnetic moment of 1.76 μ_B at 17.5 K, which decreases to 1.52 μ_B at 300 K, consistent with a spin-only value (1.73 μ_B) for one unpaired electron.

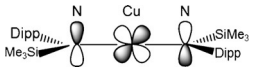
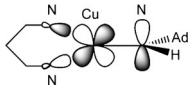
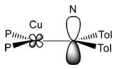
Cyclic voltammetry of **2** revealed a reversible Cu(I/II) oxidation at $E_{1/2} = -0.499$ V vs. Fc/Fc^+. Thus, **2** is less reducing than the $[Ni\{N(SiMe_3)Dipp\}_2]^-$ analogue at −1.082 V vs. Fc/Fc^+.[10]

The electronic spectrum of **1** ($^2D_{5/2}$ ground state) in hexanes at 25 °C shows strong absorptions at 210 nm and 240 nm with ε values of about 90000 L mol^{-1} cm^{-1} and 25000 L mol^{-1} cm^{-1}. Lower intensity absorptions were observed at 640, 880, and 960 nm with extinction coefficients of 200, 700, and 400 L mol^{-1} cm^{-1}, respectively. These maxima correspond to the differences between the calculated energies of the 3d orbitals (see the Supporting Information).

The absence of zero-field splitting in **1** facilitates the recording of the EPR spectrum, which is not observable in many two-coordinate complexes. The g_x ($g_\parallel$) value 2.1270 is lower than the ca. 2.20–2.30 range seen in tetragonal Cu^{II} complexes (Table 1),[9b,23] consistent with significant covalent character in the Cu^{II}–N bond. The spin delocalization onto the ligands decreases the metal character (spin population on Cu^{II} $\kappa_x \approx 0.5$) in the ground state and therefore the g value also.[9b,23]

A quartet of ^{63,65}Cu hyperfine signals (^{63}Cu, [69.17%, $I = 3/2$] and ^{65}Cu [30.83%, I = 3/2]) centered at the field position (315.0 mT) corresponding to the g_x value with splittings of approximately 8.6 mT (258 MHz or 86×10^{-4} cm^{-1}) is evident in Figure 3A. This value is comparable to that of trigonal-planar type 1 Cu site in fungal laccase *Myceliophthora thermophila* (261 MHz, corresponding to 87×10^{-4} cm^{-1}), which has a very covalent Cu–S(Cys) bond.[24] Furthermore, superhyperfine coupling with two equivalent ^{14}N nuclei ($I = 1$) gives a pattern of five hyperfine signals with an intensity ratio of circa 1:2:3:2:1, near the g_z value (corresponding to field position 333.8 mT). These features are well simulated using an anisotropic ligand hyperfine (A^{14}_N) tensor [6 6 45] MHz (Figure 3), suggesting that ligand hyperfine coupling is dominant along the g_z direction.

Table 1: EPR parameters for selected copper(II) amido complexes.

Compound	$g_1/g_2/g_3$	^{63}Cu $A_1/A_2/A_3$ [MHz]	^{14}N $A_1/A_2/A_3$ [MHz]	Spin population		Ref.
1	2.1270 2.0425 2.0076	258 54 30	ca. 6 ca. 6 45	$N(0.01_{2s},0.25_{2p})_2$[c]		this work
(nacnac)CuNHAd[a]	2.133 2.036 2.031	365 n.d.[f] n.d.	7 5 61	$N(0.01_{2s},0.33_{2p})$[c] $Cu(0.30)\ N_{amide}(0.49)$[d]		[9c]
LCu-NR_2[b]	2.030 2.008 2.008	170 34 34	24 24 100	$Cu(0.14_{3d})$[e] $N(0.03_{2s},0.45_{2p})$[c] $Cu(0.13)\ N(0.49)$[d]		[24]
blue copper site	2.226 2.059 2.047	210 n.d. n.d.	n.a.[g]	$Cu(0.41_{3d})\ S(0.38_{3p})$[e]	–	[9b]

[a] Ad = adamantyl. [b] R = *p*-tolyl; L = $[Ph_2B(CH_2P^tBu_2)_2]^-$. [c] From reported hyperfine parameters. ^{14}N spin populations (ρ_i) calculated using a_{iso} = 1811 MHz and P = 138.8 MHz[25] and the equations $A_{iso} = \rho_{2s}a_{iso}$, $A_{dip} = [T, T, -2T]$, and $T = -2/5\rho_{2p}P$. [d] From DFT results. [e] From XAS. [f] Not determined. [g] Not applicable.

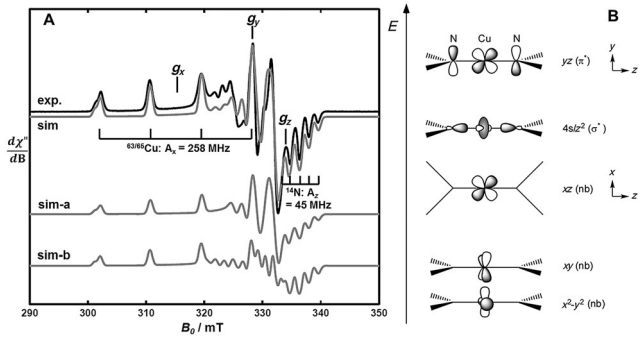


Figure 3. A) X-band CW EPR spectra of a frozen solution of **1** in hexanes (ca. 2 mM) at 30 K with 0.063 mW power (no saturation, black trace). Two-component simulation is shown in gray trace using major component (70%) of linear Cu^{II} complex (sim-a) and minor component (30%) of another similar Cu^{II} complex in hexane (sim-b). Simulation parameters for the major linear Cu^{II} complex are as follows: g = [2.1270 2.0425 2.0076], A^{63}_{Cu} = [258 54 30] MHz and two nitrogen interactions with A^{14}_{N} = [6, 6, 45] MHz. See the Supporting Information. B) Representation of the ligand field orbitals of **1**.

In summary, a two-coordinate copper(II) complex has been isolated for the first time. Its synthesis and marginal stability arise from a disproportionation of an undefined Cu^I intermediate and the dispersion force attraction between the $^-N(SiMe_3)Dipp$ ligands. A two-coordinate bis(amido) copper(I) anion salt **2** was also synthesized, allowing comparison of the effects of changing the oxidation state. The recognition that van der Waals forces can affect not only structure and stability, but can induce disproportionation[5c,27] may have application in the synthesis of new species.

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Keywords: copper · dispersion effects · disproportionation · EPR spectroscopy · silylamide

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