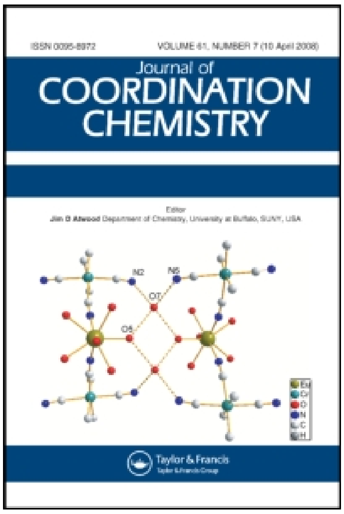

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DEFINITIVE EVIDENCE FOR SIMPLE DIAMINE COPPER(I) COMPLEXES

D. A. Haitko[a]
[a] General Electric Corporate Research and Development, Schenectady, New York, U.S.A.

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Communication

DEFINITIVE EVIDENCE FOR SIMPLE DIAMINE COPPER(I) COMPLEXES

D.A. HAITKO

General Electric Corporate Research and Development, P.O. Box 8, Schenectady, New York 12301, U.S.A.

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We wish to present new synthetic and structural evidence for the existence of two copper(I) complexes: *N, N'*-diisopropylethylenediaminecopper(I) bromide, DIEDCuBr, (*1*), which adopts a three-coordinate planar geometry and the *N, N'*.-diisopropylethylenediaminecopper(I) iodide dimer, $[\text{DIEDCuI}]_2$, (*2*), which exhibits pseudo-tetrahedral geometry about each copper in addition to a copper(I)-copper(I) interaction. The aforementioned complexes represent the first of a series[1] of classical Werner coordination compounds involving diamine ligands in copper(I) halide complexes. These complexes have been previously uncharacterized due to their extreme air and moisture sensitivity.[2] The preponderance in the literature of copper(I) complexes coordinated to unsaturated nitrogen ligands rather than amino groups is based on the expected instability of the latter due to disproportionation.[3] Stability of saturated nitrogen ligands coordinated to copper(I) has been achieved by the presence of strongly π-acidic groups such as carbon monoxide[4] and isocyanide ligands.[5] This preliminary communication will demonstrate that strongly π-acidic groups are not essential toward the stabilization of copper(I) halide compounds and that the hitherto elusive[6] diamine copper(I) halide complexes can be successfully characterized.

Addition of 1.5 mol equivalents of *N, N'*-diisopropylethylenediamine to a solution of cuprous bromide or cuprous iodide in refluxing acetonitrile followed by slow recrystallization at room temperature affords colorless crystals of (*1*) or (*2*), respectively.[7]

A colorless prismatic crystal of DIEDCuBr of dimensions 0.20 × 0.20 × 0.30 mm was mounted in a glass capillary and examined on an Enraf Nonius CAD4 diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54184Å). The monoclinic cell parameters are a = 7.650(4), b = 8.792(2), c = 19.402(5)Å, β = 96.50(3)°, Z = 4 with a calculated density of 1.47 g/cm^3, and the space group was determined to be *C2/c*. A total of 1476 reflections were collected of which 728 were used in the final analysis ($F_0^2 > 3.0\sigma(F_0)$). An absorption correction (μ = 61.3 cm^{-1}) was applied to all data. The two heavy atoms were located from an E-map and remaining atoms were located in successive difference Fourier syntheses. Full-matrix least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms and isotropically refined hydrogen atoms yielded the final agreement factors of R = 0.067 and R_w = 0.084. An ORTEP diagram of the molecule is shown in Figure 1. The structure consists of discrete monomeric units which possess crystallographic C_2 symmetry. The overall geometry about the copper atom is pseudo-trigonal-planar with the deviation from true trigonal planar geometry (all angles about copper equal to 120°) exhibited in N-Cu-N bond angle of 85.0° and equivalent Br-Cu-N bond angles of 137.5°. The copper atom lies exactly in the plane formed by the two nitrogen and bromine atoms.[8]

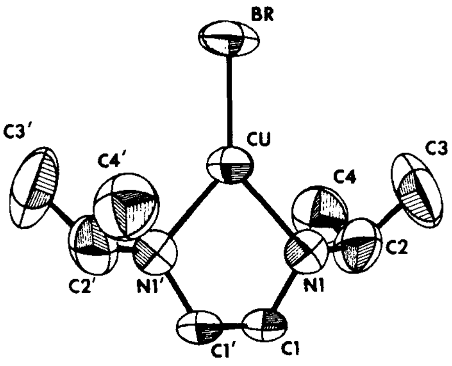

FIGURE 1 ORTEP Diagram of the nonhydrogen atoms of the DIEDCuBr molecule showing thermal ellipsoid probability of 50%.

The three-dimensional X-ray crystallographic analysis of (*2*) was solved similarly to that of the bromide derivative. A colorless crystal of (*2*) having dimensions of 0.15 mm N 0.25 mm x 0.30 mm was mounted in a glass capillary and data collection was performed with Mo Kα radiation (λ = 0.71073Å). The space group was identified as $P2_1/c$ with monoclinic cell parameters and calculated volume being a = 14.286(2), b = 11.349(5), c = 15.449(5)Å, β= 95.46(3)^3, V= 2493.4Å^3. The calculated density was 1.78 g/cm^3. Of the 5597 reflections collected, 3708 with ($F_0^2 > 3.0\sigma(F_0^2)$) were ultimately used in the analysis. The absorption coefficient is 42.8 cm^{-1}. A correction was applied to all data. A full-matrix least-squares refinement with all non-hydrogen atoms having anisotropic thermal parameters (hydrogen atoms were refined isotropically) converged to the final agreement factors of R = 0.030 and R_w = 0.038. An ORTEP diagram of the molecule is given in Figure 2.^{9} Unlike DIEDCuBr, (*2*) exists as a dimer with iodine nuclei bridging the two tetrahedrally coordinated copper(I) centers. Examination of the structure reveals several interesting features including the presence of an intramolecular copper-copper interaction of 2.73Å,^{10} and a symmetrical but not the most sterically relieving orienta-

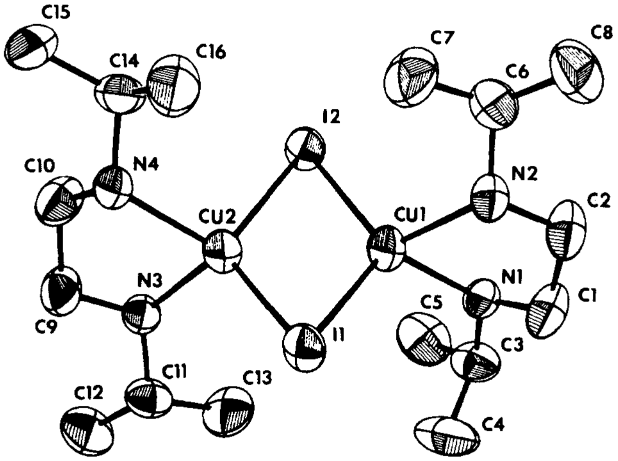

FIGURE 2 ORTEP Diagram of the nonhydrogen atoms of the [DIEDCuI]$_2$ dimer showing 40% probability ellipsoids.

tion of the isopropyl groups, since those isopropyl groups associated with N4 and N2 are oriented below the planes formed by N4, Cu2, and N3 and N2, Cu1, and N1, respectively.[11] It is interesting to note the twisting of the isopropyl group bound to N1 such that the methyl carbons C4 and C5 lie equidistantly to C13. This destroys all symmetry in the molecule. The overall geometry about each copper(I) center is tetrahedral with asymmetrically bridging iodine nuclei (Cu1-I1 = 2.661(1)Å, Cu1-I2 = 2,581(1)Å, Cu2-I1 = 2.579(1)Å, and Cu2-I2 = 2.666(1)Å). The irregularity about each copper(I) is also apparent upon examining the inequivalence of the N-Cu-I angles (N2-Cu1-I1 = 101.8(1)°, N2-Cu1-I2 = 117.8(1)°).

To our knowledge, compounds (*1*) and (*2*) represent the first simple copper(I) halide complexes coordinated to "hard" diamine ligands. It is noteworthy that each complex has unusual structural features. Compound (*1*) adopts the rare three-coordinate planar coordination geometry for copper(I) and (*2*) exhibits a copper(I)-copper(I)-interaction of 2.73Å. Studies are in progress in order to determine the factors goverining monomer *versus* dimer formation for complexes of this type.[1] Solutions of these complexes appear blue upon introduction of oxygen and revert to their original colorless appearance upon purging with nitrogen thus indicating the potential of these complexes for intermediary oxygen coordination and activation.[12] Further investigations are in progress. Tables of positional and thermal parameters and structure factors (30 pages) have been deposited with the editor and are available upon request.

ACKNOWLEDGEMENT

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7. Due to the extreme air and moisture sensitivity of these complexes, Schlenk techniques were used throughout the analyses. ^{1}H NMR data recorded at 200 MHz in acetonitrile-d_3 (all δ in ppm relative to Me_4Si) for DIEDCuBr: $\delta((CH_3)_2CH)$ 2.94, (*m*, J_{HH} = 6.5 Hz), $\delta((CH_3)_2CH)$ 1.80, (d, J_{HH} = 6.5Hz), δ(N-*H*) 2.43, $\delta(\text{-N-}CH_2CH_2\text{N-})$ 2.70; [DIEDCuI]$_2$ (monomer): $\delta((CH_3)_2CH)$ 3.00, (*m*, J_{HH} = 7.0 Hz), $\delta((CH_3)_2CH)$ 1.22, (d, J_{HH} = 7.0 Hz), δ(N-H) 2.41, $\delta(\text{-N}CH_2CH_2\text{N-})$ 2.72. Anal. Calcd for $C_8H_{20}N_2CuBr$: C, 33.40; H, 6.96; N, 9.74; Br, 27.80%. Found: C, 33.29; H, 6.90; N, 9.63; Br, 28.03%. Calcd. for $C_8H_{20}N_2CuI$: C, 28.70; H, 5.98; N, 8.37; I, 37.96%. Found: C, 28.68; H, 5.90; N, 8.34; I, 38.15%. Vapor phase osmometry experiments in (CH_3CN) for DIEDCuBr: calculated 287; found 300 and for [DIEDCuI]$_2$; calculated 669; found 332: indicating a monomeric form in CH_3CN solution.
8. Pertinent bond lengths (Å) and angles (•) are as follows: Cu-Br 2.263(2), Cu-N1 2.062(6), N1-C1 1.497(8), N1'-C2 1.524(10), C1-C1' 1.522(14), C2-C3 1.564(13), and C2-C4 1.522(13); Br-Cu-N1 137.5(2), N1-Cu-N1'85.0(4), Cu-N1-C1 108.0(4), Cu-N1-C2 120.0(6), C1-N1-C2 109.4(7), N1-C1-C1' 109.2(5), N1-C2-C3 102.2(0), N1-C2-C4 112.4(7), and C3-C2-C4 110.4(9).

9. Pertinent bond lengths (Å) and angles (•) are as follows: I1-Cu1 2.661(1), I1-Cu2 2.579(1) 12-Cu1 2.581(1), 12-Cu2 2.666(1), Cu1-Cu2 2.733(1), Cu1-N1 2.124(3), Cu1-N2 2.230(4) Cu2-N3 2.196(3), Cu2-N4 2.144(3), N1-C1 1.455(7) N1-C3 1.475(6), N2-C2 1.467(6), N2-C6 1.467(6) N3-C9 1.466(6), N3-C11 1.472(5), N4-C10 1.459(6), N4-C14 1.480(5), C1-C2 1.491(8), and C9-C10 1.514(7); Cu1-I1-Cu2 62.8(6), Cu1-I2-Cu2 62.7(7), I1-Cu1-I2 116.9(4), I1-Cu1-Cu2 57.1(1), I1-Cu1-N1 116.8(1), I1-Cu1-N2 101.8(1), 12-Cu1-Cu2 60.1(3), I2-Cu1-N1 115.8(1), I2-Cu1-N2 117.8(1), Cu2-Cu1-N1 142.5(1), Cu2-Cu1-N2 134.7(3), N1-Cu1-N2 81.9(1), I1-Cu2-I2 16.8(4), I1-Cu2-Cu1 60.0(3), I1-Cu2-N3 113.4(1), I1-Cu2-N4 119.7(1), I2-Cu2-Cu1 57.1(0), I2-Cu2-N3 111.4(1), I2-Cu2-N4 107.1(1), Cu1-Cu2-N3 131.4(1), Cu1-Cu2-N4 143.7(4), N3-Cu2-N4 83.9(1), Cu1-N1-C1 103.9(3), Cu1-N1-C3 126.1(3), Cu1-N1-C3 114.2(4), Cu1-N2-C2 105.9(3), Cu1-N2-C6 119.7(3), N2-C2-C1 111.2(4) N4-C10-C9 109.9(4), C2-N2-C6 114.4(4), Cu2-N3-C9 103.7(3), Cu2-N3-C11 118.6(3), C9-N3-C11 113.5(4), C2-N4-C10 103.5(3), Cu2-N4-C14 117.8(3), C10-N4-C14 113.7(4), N1-C1-C2 111.3(4), and N3-C9-C10 111.3(4).
10. The distance between the two copper (1) nuclei of 2.73Å is within the range found for several copper (1) cluster compounds. See: V. Schramm, *Inorg. Chem.*, **17**, 714 (1978); R.R. Gagne, R.P. Kreh, J.A. Dodge, R.E. Marsh and M. McCool, *Inorg. Chem.*, **21**, 254 (1982); V. Schramm and K.F. Fisher, *Naturwissenschaft*, **61**, 500 (1974); C.L. Raston and A.H. White, *J. Chem. Soc. Dalton*, 2153 (1976); R. Hesse, *A.K. Kemi*, **20**, 481 (1962); M.R. Churchill and K.L. Kattra, *Inorg. Chem.*, **13**, 1899 (1974); R. Hoffmann and P.K. Mehrotra, *Inorg. Chem.*, **17**, 2187 (1978), and references therein.
11. The least sterically crowding orientation of the four isopropyl groups might be expected to be one in which the isopropyl groups associated with those nitrogen atoms oriented *trans* with respect to the plane formed by the four nitrogens occupy similar directions in space.
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