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A Bis-Acetonitrile Two-Coordinate Copper(I) Complex: Synthesis and Characterization of Highly Soluble $B(C_6F_5)_4^-$ Salts of $[Cu(MeCN)_2]^+$ and $[Cu(MeCN)_4]^+$

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Copper(I)–acetonitrile complexes are exceedingly useful starting materials for the synthesis of copper(I) complexes with polydentate ligands. To extend the utility of such chemistry to solution studies in relatively low-dielectric solvents (i.e., diethyl ether, toluene) and to aid in obtaining products amenable to X-ray diffraction studies, we have recently begun to employ counteranions such as $B(C_6F_5)_4^-$ for bioinorganic studies. Thus, the synthesis of $[Cu(MeCN)_4]B(C_6F_5)_4$ (**1**) is presented. Its recrystallization from CH_2Cl_2/pentane yields the linear, two-coordinate complex $[Cu(MeCN)_2]B(C_6F_5)_4$ (**2**), whose centrosymmetric X-ray structure shows that its Cu–N distance is significantly shorter than that in other two-coordinate Cu(I) complexes with nitrogen ligands or that in the tetrahedral complex $[Cu(MeCN)_4]ClO_4$. Infrared spectroscopy indicates interesting and diagnostically useful differences between the ν(CN) of **1** and **2**.

Salts of tetrakis(acetonitrile) copper(I), $[Cu(MeCN)_4]^+$,[1−5] are exceedingly useful starting materials for the synthesis of copper(I) complexes possesing polydentate ligands. For example, a wide range of nitrogen-donor ligands (e.g., pyridylalkylamine) and their chelate copper(I) complexes synthesized utilizing tetrakis(acetonitrile)copper(I) complexes $[Cu(MeCN)_4]^+(Y)$ ($Y = PF_6^-$,[1] SbF_6^-,[2] BF_4^-,[4−6] ClO_4^-)[3,4,7] have been useful in bioinorganic modeling studies of copper(I)/dioxygen chemistry.[3,8,9] To extend the utility of such chemistry from the generally used solvents dichloromethane, acetontrile, acetone, etc. to relatively low-dielectric solvents, we have recently employed fluorinated tetraarylborate anions such as tetrakis(3,5-bis-trifluoromethylphenyl)borate starting with $[Cu^I(MeCN)_4]B(C_6H_3(CF_3)_2)_4$.[10] Most recently, we have more often utilized $B(C_6F_5)_4^-$ as the counteranion, since it also affords excellent solubility (vide infra), and its cationic $[L_nCu(I)]^+$ (L = neutral ligand donor) complexes are typically easier to crystallize and result in X-ray structures less prone to problems related to disorder. Here, we describe the synthesis of $[Cu^I(MeCN)_4]B(C_6F_5)_4$ (**1**) and $[Cu^I(MeCN)_2]B(C_6F_5)_4$ (**2**). The X-ray structure of the latter is also presented, representing the first such for a linear two-coordinate bis-acetonitrile copper(I) complex. Relatively few two-coordinate copper(I) compounds with nitrogen ligands have been structurally characterized.,[11−14] especially (i) utilizing simple unidentate ligands without steric bulk[11,12] or (ii) by comparison to that of isoelectronic silver(I) and gold(I) complexes.[14,15]

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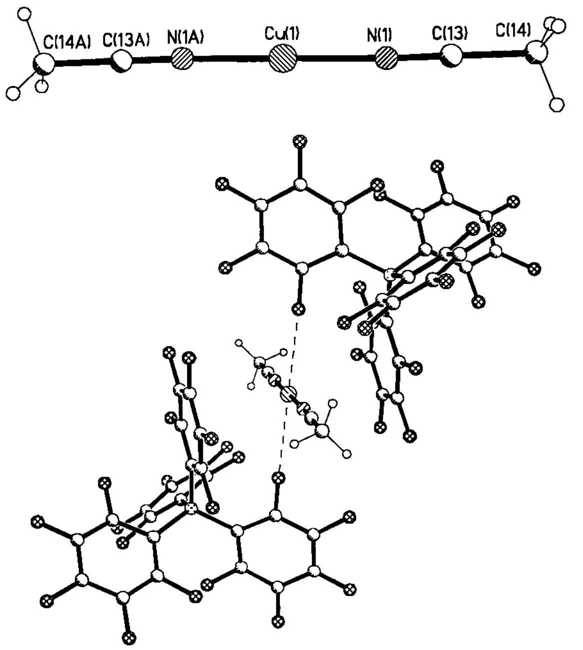

Figure 1. ORTEP diagram of [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**). (Top) The linear bis-acetonitrile copper(I) complex cationic portion with selected bond lengths and angles: Cu1−N1, 1.844 (2) Å; N1−C13, 1.131 (3) Å; ∠N1−Cu1−N1A, 180.0 (2)°. (Bottom): Diagram showing the equivalent Cu−F contacts with fluorines from the B(C$_6$F$_5$)$_4^-$ counteranion: Cu1−F5B = Cu1−F5C = 2.716 Å; ∠F−Cu−F, 180.0° (by symmetry).

[Cu$^{\mathrm{I}}$(MeCN)$_4$]B(C$_6$F$_5$)$_4$ (**1**) was synthesized by metathesis of the perchlorate salt [Cu$^{\mathrm{I}}$(MeCN)$_4$](ClO$_4$) with LiB(C$_6$F$_5$)$_4$·Et$_2$O. We also present another easy method, avoiding perchlorates and using only commerical materials (Method 2, Experimental Section). The bis-MeCN complex [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**) was generated by multiple recrystallizations of **1** from CH$_2$Cl$_2$/pentane. Both **1** and **2**, and copper complexes (which employ polydentate alkylamine/pyridine ligands) synthesized from these, are soluble in solvents such as diethyl ether and even somewhat in toluene.[16] Also, [Cu$^{\mathrm{I}}$(MeCN)$_4$]B(C$_6$F$_5$)$_4$ (**1**) and [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**), once obtained as solids, conveniently, are not particularly air-sensitive and can be handled and weighed on the benchtop.

An X-ray structure of [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**) was obtained; see the Experimental Section and Supporting Information for full details. The cationic portion (Figure 1) is the linear[11−13] MeCN−Cu$^{\mathrm{I}}$−NCMe moiety, with ∠N1−Cu1−N1A = 180.0 (2)° (centrosymmetric). The copper(I)-ligand bonding in **2** is exceptionally strong (Cu−N = 1.844 (2) Å), possessing the shortest Cu−N distance (by ~0.01−0.06 Å) yet observed for two-coordinate Cu(I) complexes ligated by two nitrogen donor ligands.[11−13] Of course, significantly longer Cu−N distances (1.99 Å average) are seen in the known tetrahedral complexes [Cu$^{\mathrm{I}}$(MeCN)$_4$]ClO$_4$[17] or bis(succinodinitrile)copper(I) perchlorate.[18] The N−C bond length of 1.131(3) Å compares to that of [Cu$^{\mathrm{I}}$(MeCN)$_4$]ClO$_4$,[17] which ranges from 1.10(2) to 1.14(2) Å. The X-ray structure of **2** also reveals additional weak copper(I)−fluorine interactions with the B(C$_6$F$_5$)$_4^-$ anion (Figure 1). Such additional or multiple weak interactions are known for linear L−M−L complexes, as with an O-atom of ClO$_4^-$ in bis(2,6-dimethylpyridine)copper(I) perchlorate,[19] C atoms (π-olefin) in bis(1-methylpyrazole)copper(I) tetrafluoroborate,[11] or fluorine atoms from "weakly" coordinating fluoroanions in a variety of other two-coordinate silver, mercury, or gold ion complexes.[20]

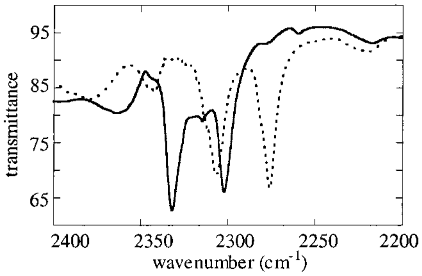

Figure 2. Overlay of the IR spectra (Nujol mull) of [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**) (—) and [Cu$^{\mathrm{I}}$(MeCN)$_4$]B(C$_6$F$_5$)$_4$ (**1**) (···).

However, these weak solid-state interactions do not appear to persist in dichloromethane solution, as judged by ^{19}F NMR spectroscopy. The *o*-, *m*-, and *p*-fluorine atoms in both [Cu$^{\mathrm{I}}$(MeCN)$_4$]B(C$_6$F$_5$)$_4$ (**1**) and [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**) show essentially identical chemical shifts (see Experimental Section for data).

Additionally, the ν(CN) of [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**) as determined by IR spectroscopy (Nujol mull) also contrasts with that of the tetracoordinate, tetrahedral complex [Cu$^{\mathrm{I}}$(MeCN)$_4$]B(C$_6$F$_5$)$_4$ (**1**). As can be seen from the overlayed IR spectra in Figure 2, the ν(CN) of **2** is 26 cm^{-1} higher (2302 cm^{-1}) than that of **1** (2276 cm^{-1}) and is a powerful characterization technique for determining the extent of MeCN loss on the copper center when recrystallizing **1** to obtain **2**. The higher energy vibration in the ν(CN) region (2331 and 2306 cm^{-1} for **2** and **1**, respectively) can be assigned to a combination band that results from the symmetrical CH$_3$ deformation and the C−C stretch that borrows its intensity from the ν(CN) band, which is a frequently observed phenomenon in acetonitrile complexes.[21−23] IR spectroscopy reveals no evidence for the formation of an intermediate tricoordinate complex "[Cu$^{\mathrm{I}}$(MeCN)$_3$]B(C$_6$F$_5$)$_4$" during the conversion of **1** to **2**.

Although complex [Cu$^{\mathrm{I}}$(MeCN)$_2$]B(C$_6$F$_5$)$_4$ (**2**) is the first structurally characterized two-coordinate Cu(I) complex ligated by two nitrile ligands, the synthesis of a [Cu(MeCN)$_2$]$^+$ complex through prolonged in vacuo treatment of [Cu(MeCN)$_4$]BF$_4$ to yield [Cu(MeCN)$_2$]BF$_4$ has been reported.[5] The ν(CN) reported for [Cu(MeCN)$_2$]BF$_4$ is 2285 cm^{-1}, which is significantly lower (17 cm^{-1}) than that observed

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for **2**. It is known from various $[Cu(MeCN)_4]^+$ complexes that varying the counteranion (SO_3Me^-,[5] $SO_3CF_3^-$,[5] BF_4^-,[5] PF_6^-,[1] ClO_4^-,[4] and now $B(C_6F_5)_4^-$) does not affect the ν(CN) in these coordinately saturated tetrakis-acetonitrile copper(I) complexes. Thus, we speculate that the discrepancy between the ν(CN) of **2** and $[Cu(MeCN)_2]BF_4$ may be explained by the fact that the BF_4^- anion may be binding or at least interacting slightly more strongly with the copper(I) ion than occurs with the $B(C_6F_5)_4^-$ counteranion in **2** to lower its ν(CN) compared to that of **2**.[24-26]

In conclusion, $[Cu^I(MeCN)_2]B(C_6F_5)_4$ (**2**), a linear, two-coordinate copper(I) compound ligated by two nitrile ligands, has been **s**ynthesized and structurally characterized. It possesses a significantly shorter Cu−N distance than $[Cu(MeCN)_4]ClO_4$, and even other two-coordinate Cu(I) complexes with nitrogen ligand donors, and its ν(CN) is 26 cm^{-1} higher than that of copper(I) tetrakis(acetonitrile) complexes. Complex **2** may serve as a useful starting material for the synthesis of copper(I) complexes, which can lead to solubility in low-dielectric solvents, and where the presence of less acetonitrile is preferred.[3,27]

Experimental Section

Materials and Methods. All reagents and solvents were purchased from commercial sources and are of reagent quality unless otherwise stated. All air-sensitive compounds were handled under an argon atmosphere using standard Schlenk techniques or in an MBraun Labmaster 130 inert atmosphere (<1 ppm O_2, <1 ppm H_2O) glovebox filled with nitrogen. Acetonitrile (CH_3CN) and methylene chloride (CH_2Cl_2) were distilled from calcium hydride, and pentane was distilled from sodium/benzophenone, all under argon. Deoxygenation of these solvents was achieved by bubbling with argon for 30 min or by three freeze/pump/thaw cycles prior to introduction into the glovebox. *Warning: Perchorlate compounds are potentially explosive! While we have experienced no problems, extreme care must be taken when working with perchorlate complexes and only small quantities should be handled.*

$[Cu^I(MeCN)_4]B(C_6F_5)_4$ (1). Method 1. To a flame dried 100 mL Schlenk flask equipped with a 125 mL addition funnel and stir bar were added $[Cu^I(MeCN)_4]ClO_4$[3] (86 mg, 0.26 mmol) and $LiB(C_6F_5)_4{\cdot}Et_2O$ (Boulder Scientific) (200 mg, 0.26 mmol, 1 equiv) under an Ar flow. In the addition funnel, 35 mL of distilled CH_3CN was added under positive Ar flow and degassed for 25 min. Addition of 3 mL of this deaerated CH_3CN to the flask yielded a clear, tan solution. After 30 min, addition of 40 mL of degassed H_2O (via Ar bubbling) to the stirring solution led to the formation of a precipitate. This tan solid was isolated via filtration under Ar (coarse porosity Schlenk filter frit) and placed under vacuum overnight, and 146 mg (61% yield) of the free-flowing, off-white solid product (**1**) was transferred into the glovebox for storage. Analysis of the noncrystalline material is as follows. ^{19}F NMR (376 MHz, CD_2Cl_2, 293 K; reference used was α,α,α-trifluorotoluene, −63.73 ppm): δ (ppm) (s, 8F, $B(C_6F_5)_4$-*m*-F) −134.18, (t, 4F, $B(C_6F_5)_4$-*p*-F) −164.34, (t, 8F, $B(C_6F_5)_4$-*o*-F) −168.34. Anal. Calcd for $C_{32}H_{12}BCuF_{20}N_4$: C, 42.39; H, 1.33; N, 6.18. Found: C, 42.48; H, 1.39; N, 5.99. IR (Nujol): 2306 (MeCN, m), 2276 (MeCN, m) cm^{-1}.

$[Cu^I(MeCN)_4]B(C_6F_5)_4$ (1). Method 2. To a 100 mL Schlenk flask equipped with a stir bar were added $[Cu^I(MeCN)_4]PF_6$ (commercially available from Aldrich or Strem Chemicals) (223 mg, 0.598 mmol), $LiB(C_6F_5)_4{\cdot}Et_2O$ (Boulder Scientific) (456 mg, 0.600 mmol), and 8 mL of deoxygenated CH_3CN under an inert atmosphere. The reaction mixture was stirred for 1 h, after which the product (**1**) was precipitated with addition of 75 mL of deoxygenated H_2O. This solid was isolated via filtration through a coarse porosity Schlenk filter frit. The product (**1**) was dried under vacuum for 12 h to give 408 mg (75% yield) as an off-white solid. ^{19}F NMR (376 MHz, CD_2Cl_2, 293 K; reference used was α,α,α-trifluorotoluene, −63.73 ppm): δ (ppm) (s, 8F, $B(C_6F_5)_4$-*m*-F) −133.80, (t, 4F, $B(C_6F_5)_4$-*p*-F) −164.38, (t, 8F, $B(C_6F_5)_4$-*o*-F) −168.26. IR (Nujol): 2306 (MeCN, m), 2276 (MeCN, m) cm^{-1}.

Synthesis of $[Cu^I(MeCN)_2]B(C_6F_5)_4$ (2). In the glovebox under N_2 was dissolved $[Cu^I(MeCN)_4]B(C_6F_5)_4$ (**1**) (0.034 g, 0.037 mmol) in ~1 mL of CH_2Cl_2, producing a clear, colorless solution with a minute amount of insoluble, tan-colored suspension. The mixture was filtered through a Kimwipe-plugged pipet to remove the insoluble solid, and the filtrate was mixed with ~5 mL of pentane to form a precipitate. The white precipitate was redissolved in ~1 mL of CH_2Cl_2, filtered, and reprecipitated again. After the reprecipitation process was repeated three times to remove previously coordinated CH_3CN that had been liberated, the white solid was dissolved in ~2 mL of CH_2Cl_2, carefully layered with ~5 mL of pentane, and left at room temperature. After 24 h, long, white needlelike crystals of $[Cu^I(MeCN)_2]B(C_6F_5)_4$ (**2**) had formed. Yield: 0.016 g, 52%. ^{19}F NMR (470 MHz, CD_2Cl_2, 293 K; reference used was α,α,α-trifluorotoluene, −63.73 ppm): δ (ppm) (s, 8F, $B(C_6F_5)_4$-*m*-F) −133.78, (t, 4F, $B(C_6F_5)_4$-*p*-F) −164.29, (t, 8F, $B(C_6F_5)_4$-*o*-F) −168.19. IR (Nujol): 2332 (MeCN, m), 2302 (MeCN, m) cm^{-1}. Anal. Calcd for ($BC_{28}CuF_{20}H_6N_2$): C, 40.78; H, 0.73; N, 3.40. Found: C, 41.09; H, 0.63; N, 3.98.

Crystallographic Structural Determination. A suitable crystal of $[Cu^I(MeCN)_2]B(C_6F_5)_4$ (**2**) for data collection was selected and mounted with epoxy cement on the tip of a fine glass fiber. Data were collected at 173 K with a Siemens P4/CCD diffractometer with graphite-monochromated Mo Kα X-radiation ($\lambda = 0.71073$ Å).

No evidence of symmetry higher than monoclinic was observed in the diffraction data. The systematic absences are uniquely consistent with the reported space group, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. The cation resides on a crystallographic inversion center, while the anion resides on a 2-fold axis of rotation. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

For $C_{28}H_6BCuF_{20}N_2$: monoclinic, *C*2/*c*, $a = 19.7183(16)$, $b = 8.2444(7)$, $c = 19.8057(16)$ Å, $\beta = 118.2620(10)°$, $V = 2835.9(4)$ Å^3, $Z = 4$, $Z' = 1/2$, $T = 173(2)$ K, $D_{calc} = 1.932$ g/cm, colorless rod, GOF = 1.178, $R(F) = 3.43\%$ for 3156 observed independent reflections ($4° \leq 2\theta \leq 56°$).

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(24) Although it was long considered a “non-coordinating anion,” the tetrafluoroborate anion has been shown in various crystal structures to be capable of binding to electron-deficient metal centers. The $B(C_6F_5)_4^-$ anion, on the other hand, has not been known to coordinate to metal centers. See ref 20.

(25) $B(C_6H_3(CF_3)_2)_4^-$ can in fact coordinate to metal ions; see ref 26.

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(27) The presence of even 1 equiv of MeCN per copper complex can have a profound influence on its O_2 reactivity. See ref 3.

A complete X-ray structure report, including an ORTEP diagram with full labeling, is provided in Supporting Information.

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Supporting Information Available: A complete X-ray structure report for $[Cu^I(MeCN)_2]B(C_6F_5)_4$ (**2**), including a diagram with full-atom labeling, Tables (1S−5S) with crystal data and structure refinement, atomic coordinates, bond lengths and bond angles, anisotropic displacement coefficients, and H-atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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