Product of a DMF Aminalization, Bis[bis(3,5-dimethylpyrazol-1-yl)(dimethylamino)methane]copper(II) Perchlorate−Bis(dichloromethane)

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Bis[bis(3,5-dimethylpyrazol-1-yl)(dimethylamino)methane]copper(II) perchlorate−bis(dichloromethane), Cu(II)-$(\mathbf{1})_2(ClO_4)_2{\cdot}2CH_2Cl_2$, **2**, is the unanticipated product of the reaction of tris(3,5-dimethylpyrazol-1-yl)methylsilane, **3**, with Cu(II)(DMF)$_4$ $(ClO_4)_2$. In the title complex, the Cu(II)$(\mathbf{1})_2$ cations exhibit a tetragonal Cu(II)N$_6$ geometry arising from coordination of four pyrazole N atoms and two tertiary amine N atoms from two bis(3,5-dimethylpyrazol-1-yl)(dimethylamino)methane ligands, **1**. The tridentate (N)$_3$ ligands **1** coordinate copper facially with one Cu−N (pyrazole) axial [Cu−N, 2.407(4) Å] and the second equatorial [Cu−N, 1.995(4) Å]; the cations exhibit crystallographic 2-fold symmetry that relates one ligand to the other. Cu(II)$(\mathbf{1})_2(ClO_4)_2{\cdot}2CH_2Cl_2$, $CuC_{28}H_{46}Cl_6N_{10}O_8{\cdot}2CH_2Cl_2$, crystallizes in the monoclinic space group $C2/c$, with $a = 26.278(5)$ Å, $b = 8.835(2)$ Å, $c = 20.655(4)$ Å, $\beta = 120.73(3)°$, $Z = 4$, and R_F $(R_{wF^2}) = 0.049$ (0.122) for 1979 observed reflections with $I > 2\sigma(I)$. Crystals of **2** are stable in dry air but hydrolyze readily to yield dimethylformamide and 3,5-dimethylpyrazole. A mechanism is proposed for the formation of complex **2** by silane-promoted aminalization (an aminal is the diaza analogue of an acetal) of dimethylformamide.

Introduction

As part of a long-term project designed to probe the structural and spectroscopic properties of the active sites of selected metalloproteins, we have prepared and characterized a variety of low molecular weight analogues.[1] A particular challenge has been to prepare pseudotetrahedral or pseudo-C_{3v} complexes of Cu(II). These geometries have smaller ligand-field stabilization energies than the commonly observed tetragonal or square-planar coordination geometries. Pseudotetrahedral Cu(II)N$_4$ complexes have been prepared using geometrically constraining ligands such as **4**, **5**, and **6**.[2] The tridentate ligand tris(3,5-diisopropylpyrazolyl)borate, **7**, has recently been used to construct pseudo-C_{3v} CuN$_3$S analogues of the type I copper metalloenzymes.[3] A neutral analogue of **7**, tris(pyrazol-1-yl)methane, **8**, has been used to prepare tetragonal and distorted octahedral M(**7**)$_2$ complexes.[4] The relatively short B−N and C−N bonds in **7** and **8** (1.43−1.65 Å) enforce small cone angles in their pseudo-C_{3v} metal complexes, leading to N−M−N angles substantially smaller than the tetrahedral angle. The goal in the present study was to prepare a neutral analogue of **7** with a longer pyrazole−bridgehead atom bond length. It was hoped that the added bond length would increase the cone angle and lead to metalloenzyme models with N−M−N angles closer to the ideal value. Tris(1-pyrazolyl)phosphine, **9**, a neutral compound with a longer ligand−bridgehead P−N bond length [1.714(4) Å],[5] also has the potential to increase the cone angle, but this ligand is not expected to form oxidatively stable Cu(II) complexes. Recently, neutral imidazole phosphines containing P−C bridgehead bonds have been reported. Structures of their Cu(I) complexes show an average P−C bond length of 1.808(19) Å.[6] The isopropylimidazole version of the phosphine in the presence of copper and oxygen undergoes hydroxylation at the tertiary carbon.[7] It is interesting to note, given the normal incompatibility of Cu(II) and phosphines,[8] that oxidation occurs at the tertiary C−H bond of the isopropyl group rather than at the bridgehead phosphorus atom. In a similar Mn complex reported by Kitajima,[9] hydroxylation of the tertiary C−H bond was suppressed by exogenous phosphine to produce the phosphine oxide. The stability of the tris(isopropylimidazolyl)phosphine[7] can be attributed to the steric bulk of the isopropyl groups, which might hinder approach of reagents at the phosphorus atom and/or to the electron-withdrawing character of the phosphine substituents.

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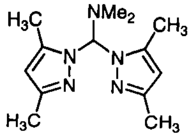

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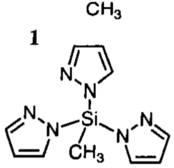
2 = title complex



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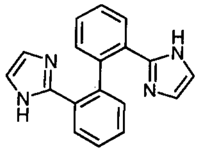

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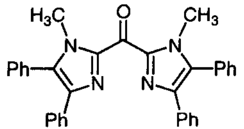

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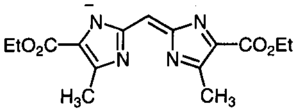

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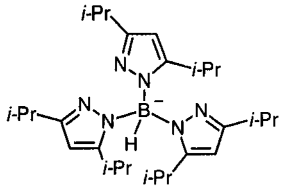

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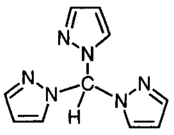

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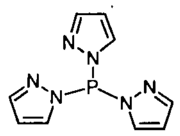

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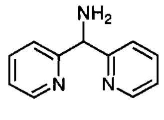

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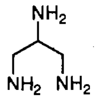
11 = Cu(II)(**10**)$_2$(ClO$_4$)$_2$



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We have prepared tris(3,5-dimethylpyrazol-1-yl)methylsilane,[10] **3**, which has a bridgehead Si−N bond length of 1.745(5) Å, with the hope of preparing a stable Cu(II) chromophore with an unusual coordination geometry. As the silane might be sensitive to hydrolysis, all manipulations were performed under inert atmosphere, and an anhydrous Cu(II) complex with labile ligands, Cu(II)(DMF)$_4$(ClO$_4$)$_2$, was chosen. The unexpected cation, Cu(II)(**1**)$_2$, is the apparent result of silane-promoted aminalization of DMF with 3,5-dimethylpyrazole. We present the preparation and X-ray structure of the title complex, **2**, as well as a proposed mechanism for its formation.

Experimental Section

General. All manipulations were conducted under nitrogen by using Schlenk and glovebox techniques. Dichloromethane and pentane were distilled from CaH$_2$. GC analyses were performed by using a HP 5890 Series II gas chromatograph. Cu(DMF)$_4$·(ClO$_4$)$_2$ was prepared by following a literature method.[11] Infrared spectra were measured by using a Mattson Galaxy Series FTIR 5000 spectrophotometer.

Synthesis of the Complex 2. A light-blue solution of 150 mg of Cu(II)(DMF)$_4$•(ClO$_4$)$_2$ (0.27 mmol) in 10 mL of dichloromethane was treated with 141 mg of **3** (0.42 mmol), whereupon the blue color intensified. In the glovebox, the flask containing the intense-blue solution was placed in a sealed container along with a flask containing pentane to allow vapor diffusion. After 12 h, the flask contained pale-green, X-ray quality crystals of **2**, which were separated from the nearly colorless filtrate. With the exclusion of atmospheric moisture, **2** is stable for more than 1 year. IR (KBr) 3265 (s), 3197 (s), 1569 (s), 1472 (m), 1412 (m), 1275 (m), 1184 (m), 1170 (m), 1144 (m), 1051 (m), 1043 (m), 1026 (m), 819 (m), 795 (m), 702 (m), 687 (m), 615 (m) cm^{-1}. An analytical sample was prepared by high-vacuum drying to remove dichloromethane. Anal. Calcd for CuCl$_2$O$_8$N$_{10}$C$_{26}$H$_{42}$: C, 41.25; H, 5.59; N, 18.50; Cu, 8.39. Found: C, 41.20; H, 5.52; N 18.56; Cu, 8.4.

Table 1. Crystal and Refinement Data for Cu(II)(**1**)$_2$(ClO$_4$)$_2$·2CH$_2$Cl$_2$[a]

formula	CuC$_{28}$H$_{46}$Cl$_6$N$_{10}$O$_8$
fw, g mol^{-1}	926.99
a, Å	26.278(5)
b, Å	8.835(2)
c, Å	20.655(4)
β, °	120.73(3)
V, Å^3	4121.9(14)
space group, monoclinic	$C2/c$
Z	4
radiation (λ, Å) graphite monochr	Mo Kα (0.710 73)
ρ_{cald}, g cm^{-3}	1.494
temp, K	293(2)
cryst size, mm	0.15 × 0.25 × 0.42
μ, mm^{-1}	0.98
data $I > 0\sigma(I)$ /restraints/param	2527/15/297
R_F (R_{wF^2})	0.049 (0.122) (1979 refs with $I > 2\sigma(I)$)
GOF	1.05

[a] Definitions: $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$; GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{par})\}^{0.5}$, with weights $w=1/[\sigma^2(F_o^2) + (0.0640P)^2 + 18.2556P]$, where $P=(F_o^2 + 2F_c^2)/3$. Additional crystallographic details are given in the Supporting Information.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.

Hydrolysis of 2. A few green crystals of **2** were suspended in 1 mL of water. After 1 h, a blue solution with some suspended buff-colored solid was obtained. The mixture was extracted with 2 mL of dichloromethane and analyzed by GC. The only products detected were DMF and 3,5-dimethylpyrazole.

X-ray Crystallography. A pale-green crystal of **2** (dimensions 0.15 mm × 0.25 mm × 0.42 mm) was coated with epoxy and mounted on the end of a glass rod. Diffraction measurements were made with an Enraf-Nonius CAD-4 diffractometer, and the data were reduced by using the Enraf-Nonius Structure Determination Package.[12] Examination of the reciprocal lattice revealed a monoclinic system with systematic absences consistent with space groups $C2/c$ and Cc. The structure was solved and refined successfully in the centrosymmetric space group $C2/c$; attempts to refine the structure in Cc led to divergence. Crystal data and additional details regarding data collection and refinement are presented in Table 1. The structure was solved by direct methods and difference Fourier techniques.[13] Refinement was full matrix on F^2.[13] Both the perchlorate anion and dichloromethane solvate molecule exhibited positional disorder, models for which were developed from an analysis of peaks in successive difference Fourier maps. For the perchlorate anion, the Cl atom was located on a single site while the O atoms occupied two sets of half-occupied sites; the C atom of the dichloromethane solvate was located on a single site, whereas each unique Cl atom was split among three sites with occupancy factors of 0.4, 0.4, and 0.2. Cl−O and C−Cl distances in these species were restrained with an esd of 0.03 Å (DFIX); relaxation of these restraints gave unrealistic geometries for these species with little change in the cation parameters. All non-H atoms were refined anisotropically. H

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Table 2. Selected Geometric Parameters (Å, deg) for $Cu(II)(\mathbf{1})_2(ClO_4)_2\cdot 2CH_2Cl_2$[a]

Cu−N(3)	2.138(4)		
Cu−N(11)	2.407(4)		
Cu−N(21)	1.995(4)		
N(3)−Cu−N(3′)	105.6(2)	N(11)−Cu−N(11′)	179.6(2)
N(3)−Cu−N(11)	73.63(14)	N(11)−Cu−N(21)	85.8(2)
N(3)−Cu−N(11′)	106.65(14)	N(11)−Cu−N(21′)	93.9(2)
N(3)−Cu−N(21)	79.2(2)	N(21)−Cu−N(21′)	98.4(2)
N(3)−Cu−N(21′)	167.4(2)		

[a] Symmetry transformations used to generate equivalent atoms: single prime (′) = $-x, y, -z + 3/2$.

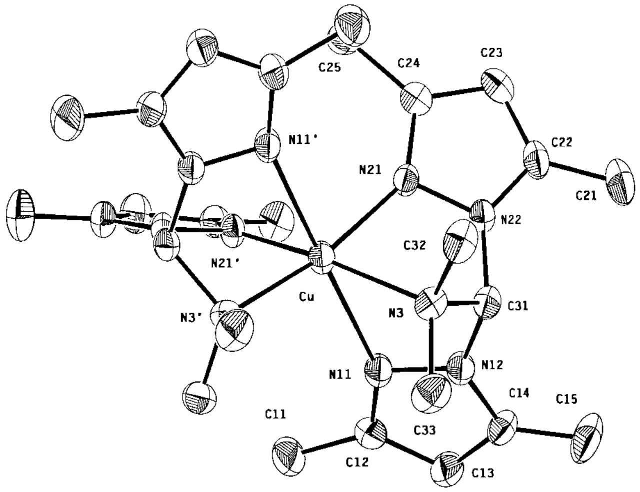


Figure 1. View (ORTEP[19]) of **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 33% probability level.

atoms were either located on difference Fourier maps or placed at calculated positions; cation H atom coordinates were refined. Selected bond distances and angles are given in Table 2. A view of the cation is shown in Figure 1.

Results and Discussion

The structure consists of Cu(II)(**1**)$_2$ cations along with perchlorate anions and dichloromethane molecules of solvation. In the cations, two tridentate (N)$_3$ ligands, **1**, coordinate Cu(II) facially to comprise a tetragonal coordination sphere. One ligand is unique and is related to the second by a crystallographic diad axis that passes through the Cu atom and bisects the N(3)−Cu−N(3′) angle. The tertiary amine N atom, N(3), and one of the pyrazole N atoms, N(21), bind equatorially, while the second pyrazole N atom, N(11), coordinates axially. Ligation by a pyrazole ring in the axial position gives rise to one six- and one five-membered ring between axial and equatorial sites, a less strained situation than two five-membered rings that would result from having the dimethylamino nitrogen axial. This observation is similar to that reported for the related Cu(II)-(**10**)$_2$ cations in Cu(II)(**10**)$_2$(ClO_4)$_2$, **11**.[14] In contrast to **2**, **11** was prepared directly from its ligand, **10**, which was synthesized by following a published procedure.[15] Complex **11**, although crystallized from water, was also found to be hydrolytically unstable, decomposing at ambient temperature over a period of 3 days.[14] Since a pyrazole N atom of **1** coordinates axially, two isomers, rac and meso, are possible (Figure 2), corresponding to the amine N atoms cis or trans in the equatorial plane, respectively. For **2**, only the rac isomer was observed, whereas for **11**, the meso isomer formed exclusively. Crystallization of a single isomer does not preclude a rac−meso equilibrium in solution from which the less soluble (though not necessarily thermodynamically more stable) isomer precipitates. Such equilibria have been observed for metal complexes of **10**[14] and of **12**.[16]

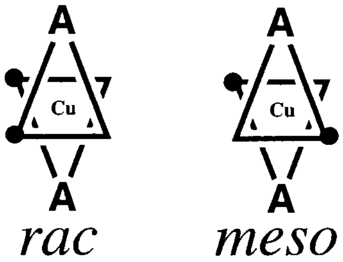
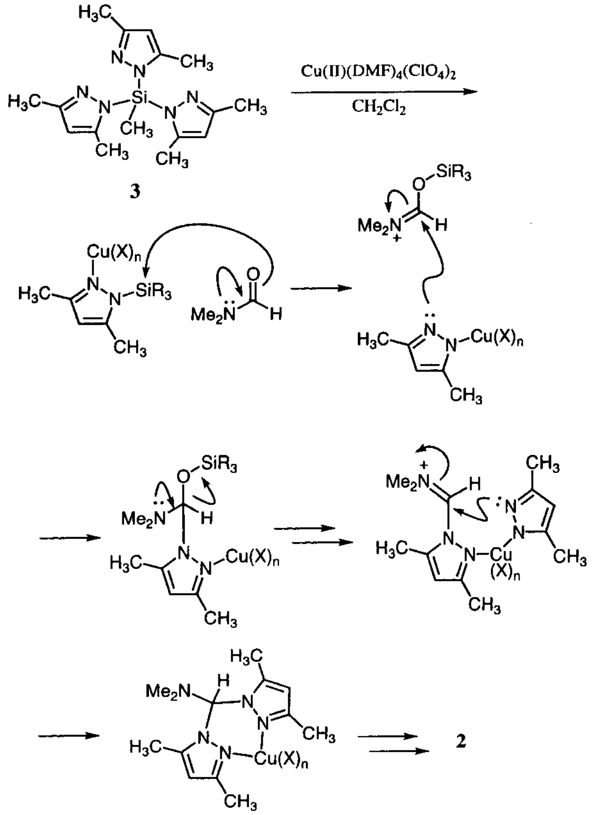


Figure 2. Sketch showing ligand placement for the rac and meso isomers of **2**. “A” corresponds to an apical position and the dots represent the dimethylamino N atoms.

Scheme 1. Proposed Mechanism for Formation of **2**



An unusual aspect of **2** is its direct formation from Cu-(DMF)$_4\cdot$(ClO_4)$_2$ and **3**. A possible mechanism for this reaction, beginning with coordination of N-2 of a 3,5-dimethylpyrazole component of **3** to Cu(II), and then O-silylation of DMF by the Cu-activated species, is shown in Scheme 1. O-Silylation of DMF with electrophilic silanes is well precedented.[17] The remainder of the mechanism follows a standard DMF acetalization route,[18] with Cu(II)-activated pyrazole taking the place of the alcohol. Cu(II) may also play a role in delivering the

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second pyrazole and in stabilizing the closed form (an aza-ortho ester) with respect to the open form (an amidinium salt).

The facile preparation of **2** from DMF and pyrazolylsilane **3** in the presence of Cu(II) suggests that the Si−N (pyrazole) bond is fairly reactive, complicating efforts to obtain a neutral Cu(II) analogue of **7** with a long Si(bridgehead)−N bond. The question remains as to whether ligand **3** can be used with Cu(II) sources not containing DMF to obtain the desired N-silylated tris(pyrazol-1-yl) Cu(II) complex. Thus far, attempts to form suitable crystalline complexes of **3** with other copper(II) salts have not been successful. Perhaps the lability of the Si−N (pyrazole) linkage will limit the use of this ligand to less active metal ions. It is expected that the Si−C bond length in tris(imidazol-2-yl)silane will be similar in length to the Si−N (pyrazole) bond.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, of the structure of bis[bis(3,5-dimethylpyrazol-1-yl)-(dimethylamino)methane]copper(II) perchlorate−bis(dichloromethane), **2**, is available on the Internet only. Structure factors can be obtained by contacting the authors. This material is available free of charge via the Internet at http://pubs.acs.org.

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