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Article

FOX-7 (1,1-Diamino-2,2-dinitroethene): Trapped by Copper and Amines

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Syntheses of the first $Cu(NH_3)_2(FOX)_2$ and various $Cu(amine)_2(FOX)_2$ (methyl, propyl, and dimethyl amine) complexes were achieved by using metathetical reactions which add a new chapter to the metal chemistry of FOX-7 (1,1-diamino-2,2-dintroethene). The crystal structures of $Cu(NH_3)_2(FOX)_2$ and $Cu(C_3H_7NH_2)_2(FOX)_2$ which show square planar geometry at copper aid in the understanding of the bonding modes in FOX-7 copper complexes which is supported by natural bond orbital (NBO) calculations. Water-free K-FOX was also structured.

Introduction

Development of new and improved energetic materials has long been an area of continuing interest among researchers.[1−3] Much attention is focused on designing energetic molecules which exhibit good balance between sensitivity and performance.[4,5] Recently 1,1-diamino-2,2-dinitroethene, FOX-7, has attracted significant interest because of its potentially high performance, thermal stability, and low sensitivity to impact and friction.[6−8] A constant effort is being made to improve and enhance its performance through optimizing and modifying its structure by forming different derivatives.[5,9,10] FOX-7 is an ethene, and the presence of two electron donating amino groups on one carbon and two electron withdrawing nitro groups on the other carbon greatly influences its reaction chemistry. The positive charge assigned to the amino-substituted carbon encourages transamination reactions resulting in mono- and disubstituted dinitroethenes.[11,12] However, reaction of FOX-7 with liquid ammonia, gave mainly guanidinium dinitromethanide with a small amount of ammonium cyanodinitromethanide.[5] With guanidine, deprotonation of FOX-7 gave its guanidium salt rather than a transamination product which demonstrates another reaction mode displayed by FOX-7.[10,12] The chemical reactivity of FOX-7 toward electrophiles (e.g., *N*-chlorosuccinimide, acetyl chloride, isocyanatohexane) resulted in its amino substituted derivatives.[13] While FOX-7 with cold aqueous KOH gave white crystalline potassium salt, K-FOX, at 70 °C hydrolytic cleavage of the C═C bond

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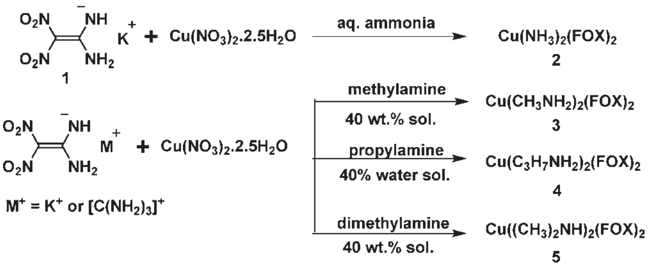
Scheme 1. Reactions of G-FOX or K-FOX with Copper Ion in the Presence of Ammonia or Primary Amines



resulted in the formation of potassium dinitromethanide.[8,12] Recently, our group successfully synthesized the silver salt of FOX-7 along with silver-ammonia-FOX and silver-amine-FOX compounds which are unique examples in the coordination chemistry of FOX-7.[14]

Now we describe some exciting new compounds which are the first examples of copper ammonia/amine compounds of FOX-7 and which were confirmed via single crystal X-ray structuring. Also, we report the X-ray structure of anhydrous K-FOX for comparison with K-FOX$\cdot$H$_2$O which appeared while this work was underway.[15]

Results and Discussion

A clear green solution was obtained when freshly synthesized K-FOX, **1**,[10] was stirred with $Cu(NO_3)_2\cdot 2.5H_2O$ in aqueous ammonia at room temperature (Scheme 1). Upon standing overnight, $Cu(NH_3)_2(FOX)_2$, **2**, (63% yield) appeared as purple crystals, and the solution had become blue. Interestingly, it was observed that when these crystals were left in contact with the solution for 1−2 days, they were transformed into the yellow crystals of FOX-7 likely a result of slow hydrolysis. This demonstrates that FOX-7 is a weaker coordinating ligand than ammonia and therefore is easily replaced in the coordination sphere of the metal. When guanidine FOX, G-FOX,[8] was used rather than K-FOX, only FOX-7 was formed. Different amines were reacted to determine the impact on the coordination mode of the FOX ligand with copper as a function of the amine. The reaction of K-FOX or G-FOX in methylamine and dimethyl amine (40 wt % amine) with $Cu(NO_3)_2\cdot 2.5H_2O$ gave **3** (71% yield) and **5** (67% yield) as brown solids. With propylamine, a 40% amine aqueous solution was first prepared and then used as reaction medium for the reaction of K-FOX or G-FOX with $Cu(NO_3)_2\cdot 2.5H_2O$ to obtain **4** (61% yield) as a green solid. Green crystals were obtained by dissolving the compound in a propylamine:water (80:20) mixture. All of these compounds **1**−**5** are soluble in dimethylsulfoxide (DMSO).

Suitable light yellow crystals of K-FOX, **1**, (Figure 1) were obtained by reacting FOX-7 with cold aqueous KOH solution and then adding a huge excess (50−60 mL) of methanol.

Compound **1** crystallizes in the monoclinic crystal system (space group $P2_1/c$) containing four molecules per unit cell as compared with triclinic (space group P_1) for K(FOX)$\cdot$H$_2$O.[15] In the X-ray structure of **1**, the C1−C2 bond length (1.49 Å) is close to the normal C−C single bond, similar to the salt G-FOX,[16] Ag-ammonia-FOX,[14] and K(FOX)$\cdot$H$_2$O (1.50 Å) crystals.[15] The C1−N4 bond (1.27 Å) distance is found to be shorter than the C1−N3 bond (1.35 Å) distance supporting the double bond character of the C1−N4 bond. This demonstrates that the negative charge is delocalized over the N4, C1, and C2 atoms of the molecule. The molecular geometry of the carbon and the amino nitrogen atoms is essentially planar with nitro groups twisted perpendicularly out of the plane with an average torsion angle of 89.5°. The intermolecular amino-nitro-hydrogen bonding links the FOX-7 anion into a 3D network [N3$\cdots$O10#1 = 3.042(2); N3$\cdots$O10#2 = 3.236(2) Å; Symmetry transformation #1 = $x - 1, y, z$; #2 = $-x - 1, -y + 1, -z + 3$].

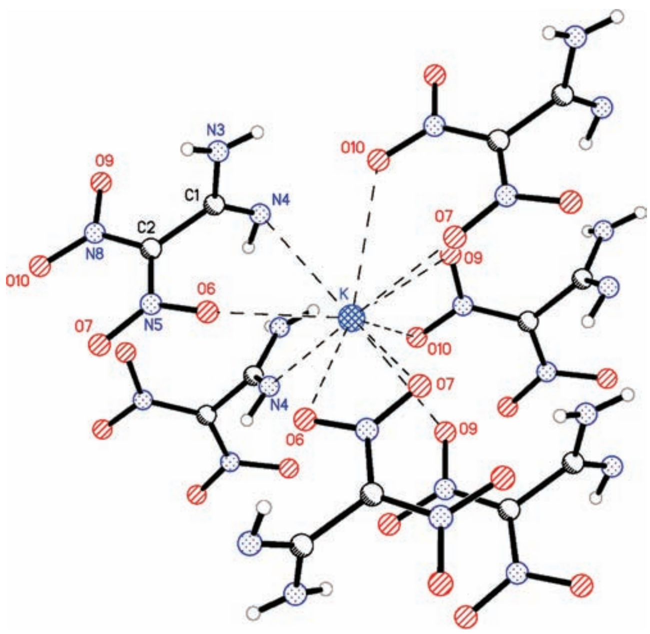


Figure 1. Crystal structure of the FOX anion in **1** (displacement ellipsoids shown at 50% probability) with coordination around the potassium atom. Selected distances [Å] and angles [deg]: C1−N4, 1.274(2); C1−N3, 1.350(2); C1−C2, 1.496(2); C2−N8, 1.361(2); C2−N5, 1.378(2); N5−O7, 1.238(2); N5−O6, 1.258(2); N8−O10, 1.251(2); N8−O9, 1.262(2); N4−C1−N3, 122.13(1); N4−C1−C2, 123.97(1); N3−C1−C2, 113.90(1); N8−C2−N5, 122.13(1); N8−C2−C1, 119.58(1); N5−C2−C1, 118.18(1); O7−N5−O6, 120.43(1); O7−N5−C2, 123.40(1); O6−N5−C2, 116.15(1); O10−N8−O9, 120.16(1); O10−N8−C2, 123.56(1); O9−N8−C2, 116.28(1).

Appropriate crystals of **2** were analyzed using X-ray diffraction. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Figure 2).

The $Cu(NH_3)_2(FOX)_2$, **2**, exhibits a square planar coordination geometry with four N-atoms (two from ammonia and two from FOX-7) coordinated in the equatorial plane. The copper atoms are located on the center of inversion, with cis angles [N3−Cu−N11#1 = 90.27(7)°; N3#1−Cu−N11#1 = 89.73(7)°; N3−Cu−N11 = 89.73(7)°; N3#1−Cu−N11 = 90.27(7)°] and trans angles (N3−Cu−N3#1 = 180.0°; N11#1−Cu−N11 = 180.0°) showing no tetrahedral distortion. The Cu−N bond length for ammonia nitrogen (2.019 Å) is comparable to amino nitrogen of FOX-7 ligand, which is a

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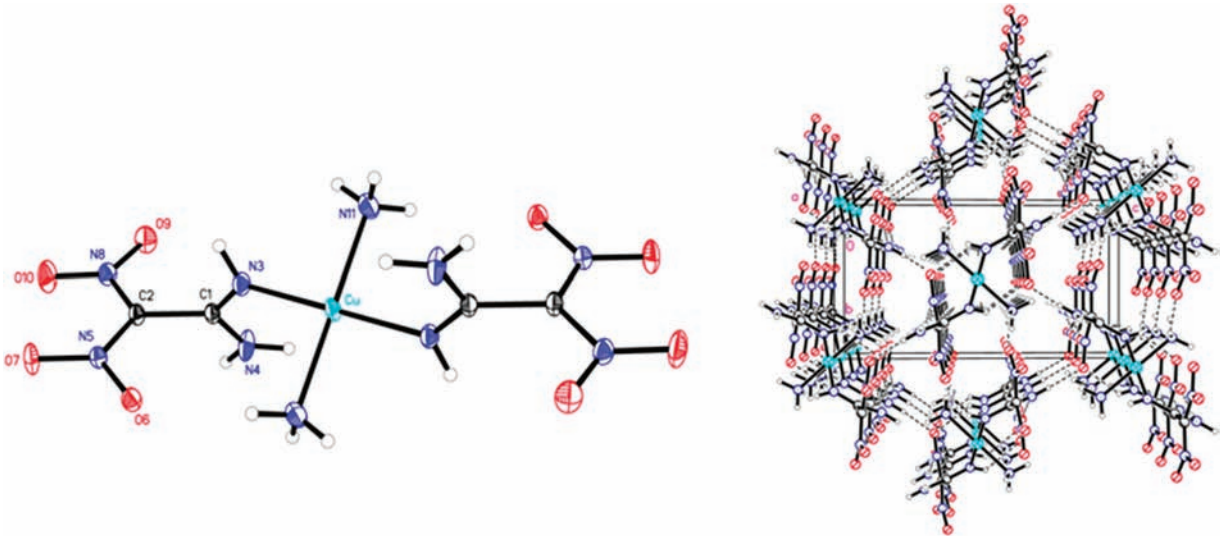

Figure 2. (1) Left: Asymmetric unit of crystal structure of **2** (displacement ellipsoids shown at 50% probability). Selected distances [Å] and angles [deg]: Cu−N3, 2.002(2); Cu−N11, 2.012(2); C1−N3, 1.286(2); C1−N4, 1.321(3); C1−C2, 1.490(2); C2−N5, 1.355(2); C2−N8, 1.490(2); C2−N5 1.355(2); N5−O7, 1.259(2); N5−O6, 1.265(2); N8−O9,1.233(2); N8−O10, 1.235(2); 7); N3−Cu−N11, 89.73; N3−C1−N4, 122.84(2); N3−C1−C2, 120.85; N4−C1−C2, 116.20(2); N5−C2−N8, 122.06(1); N5−C2−C1, 117.23(1); N8−C2−C1, 120.71(1); C1−N3−Cu, 131.37(1); O7−N5−O6, 118.97(1); O7−N5−C2, 124.00(2); O6−N5−C2, 117.03(1); O9−N8−O10, 122.48(2); O9−N8−C2, 115.72; O10−N8−C2, 121.78(2). (2) Right: Packing diagram of **2**.

typical Cu−N coordination bond length for copper complexes such as$[Cu(NH_3)_4(NO_3)_2]$.[17] Because of steric hindrance, FOX ligands are twisted out of the square equatorial plane [N11−Cu−N3−C1 = 122.95(2)°]. The C1−C2 bond distance (1.49 Å) of the FOX ligand bonded to the Cu(II) atom is nearly the same as the typical C−C single bond. The Cu bonded amino nitrogen C1−N3 bond length (1.28 Å) is shorter than the free amino nitrogen C1−N4 bond length (1.32 Å) The two nitro groups of the FOX ligand are strongly twisted out of the plane [N3−C1−C2−N8 = 110.9(2)°] likely because of strong electrostatic repulsion between the oxygen atoms of the nitro groups. One of the nitrogen atoms (N8) of the nitro groups is bonded to the C2 carbon with a slightly longer bond length (ca. 0.13 Å) as compared to the other (N5). The packing of **2** is formed by extensive amino-nitro intermolecular hydrogen bonding. In addition, the hydrogen atoms of the coordinating ammonia molecules form strong hydrogen bonds to the nitro oxygen atoms (O9 and O10) which may be destabilizing.

As was the case for **2**, $Cu(C_3H_7NH_2)_2(FOX)_2 \cdot H_2O$, **4** (Figure 3) crystallizes in the monoclinic space crystal system having the $P2_1/n$ space group with four molecules per unit cell. Compound **4** also exhibits square planar geometry with a Cu(II) atom occupying the center. The planar geometry is slightly distorted as the copper atom lies slightly above the average plane [N3A−Cu−N3B = 173.31(7)°; N11B−Cu−N11A = 175.49(9)°] with two ligating nitrogen atoms from propylamine (Cu−N11B = 2.018(2) Å; Cu−N11A = 2.025(2) Å) and two from the FOX moieties (Cu−N3A = 1.973(2) Å; Cu−N3B = 1.981(2) Å). As in **1**, the FOX ligands are also twisted out of the equatorial plane [N11B−Cu−N3A−C1A = −99.7(2)°; N11A−Cu−N3A−C1A = 75.8(2)°]. In **4**, the FOX ligands exhibit nearly the same molecular configuration with a C1−C2 bond length (1.48 Å) close to a single bond and substituted amino nitrogen N3 forming a shorter bond with the C1 carbon atom as compared to the unsubstituted amino group (ca. 0.04 Å). In contrast to **2**, both the nitro groups are bonded to the C2 carbon atom with almost the same bond lengths [C2B−N5B = 1.360(2) Å; C2B−N8B = 1.388(3) Å] and are twisted almost perpendicularly [N4B−C1B−C2B−N5B = −78.6(2); N4A−C1A−C2A−N5A = 93.5(2)] to the plane containing C1, C2 and the amino groups. The water of crystallization also forms hydrogen bonds with the oxygen atoms (O7B, O10B) of the nitro groups. Addition of water was necessary to produce a crystal of **4** for structural analysis.

The differential scanning calorimeter (DSC) measurements (Figure 4) for compounds **2** and **3** show intense exothermic peaks at 166.8 and 163.2 °C, respectively. For compounds **4** and **5**, a small endothermic peak appears before decomposition at 128.6 and 169.9 °C, respectively. Among all the compounds $Cu(C_3H_7NH_2)_2(FOX)_2$, **4** has the lowest thermal stability. Compounds **2**−**5** were tested for impact sensitivity with a BAM Fallhammer;[18] **2** was the most sensitive to impact (> 5J) whereas **3**(> 12 J), **4**(> 15 J), **5**(> 15J) were relatively less sensitive. It is difficult to predict or to rationalize impact sensitivity or the differences in impact sensitivity between similar compounds. In cases where water of crystallization molecules are present, for example, **4**, the additional hydrogen bonding may enhance compound stability while lowering the thermal stability. In **2**, strong intramolecular bonding between NH_2 and NO_2 (N8−O9 and N8−O10) may reduce the efficacy of intermolecular bonding and thus destabilize.

Natural bond orbital (NBO) population analysis was used to investigate the bonding and hybridization in **2** (Figure 5). The NBO calculation and the geometry optimization of the structures and frequency analyses were carried out using B3LYP/3-21G and MPW1PW91/SDD methods, respectively. The optimized structures were characterized as true local energy minima on the potential

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(18) (a) www.bam.de; (b) A 20 mg portion of each of the copper-amine-FOX compounds, 2−5, was subjected to a Bam Fallhammer test using a 5 or 10 kg weight: Insensitive > 40 J; less sensitive ≥35 J; sensitive ≥4 J.; very sensitive ≤3 J.

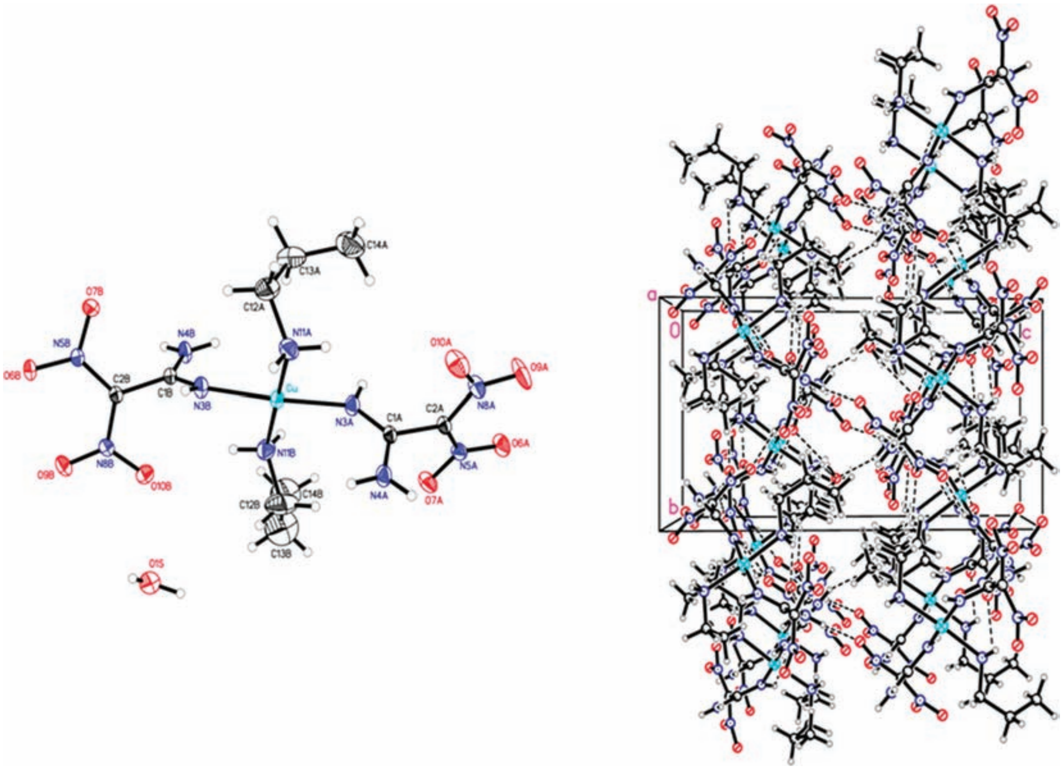

Figure 3. (1) Left: Molecular structure of **4** (displacement ellipsoids shown at 50% probability) with one molecule water of crystallization. Selected distances [Å] and angles [deg]: Cu−N3A, 1.973(2); Cu−N11A, 2.025(2); C1A−N3A, 1.286(2); C1A−N4A, 1.330(3); C1A−C2A, 1.489(2); C2A−N5A, 1.361(3); C2A−N8A, 1.381(3); N5A−O7A, 1.252(2); N5A−O6A,1.256(2); N8A−O9A, 1.230(2); N8A−O10A, 1.250(2); N11A−C12A, 1.470(4); C12A−C13A, 1.490(4); N3A−Cu−N11A, 90.43(8); N3B−Cu−N11A, 91.89(8); N11B−Cu−N11A, 175.49(9); N3A−C1A−N4A, 123.62(2); N3A−C1A−C2A, 120.39(2); N4A−C1A−C2A, 115.99(2); N5A−C2A−N8A, 123.08(2); N5A−C2A−C1A, 119.38(2); N8A−C2A−C1A, 117.53(2); C(1A)−N(3A)−Cu, 133.80(2); O7A−N5A−O6A, 120.29(2); O7A−N5A−C2A, 116.74(2); O6A−N5A−C2A, 122.97(2); O9A−N8A−O10A, 121.07(2); O9A−N8A−C2A, 123.56(2); O10A−N8A−C2A, 115.37(2); C(12A)−N(11A)−Cu, 118.15(2); N(11A)−C(12A)−C(13A), 112.0(2). (2) Right: Packing diagram of **4**.

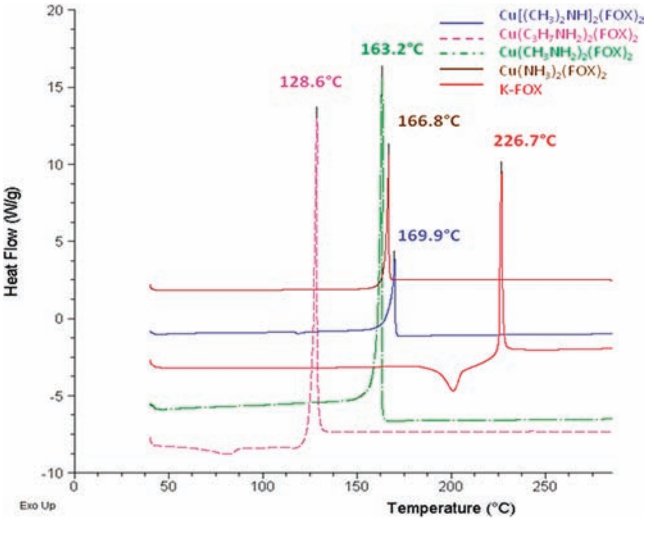

Figure 4. DSC thermograms for potassium-FOX (**1**), copper(ammonia)$_2$-(FOX)$_2$ (**2**), copper(methylamine)$_2$(FOX)$_2$ (**3**), copper(propylamine)$_2$-(FOX)$_2$ (**4**), and copper(dimethylamine)$_2$(FOX)$_2$ (**5**).

energy surface without imaginary frequencies. The calculations were carried out using the Gaussian 03 suite of programs (revision D.01).[19]

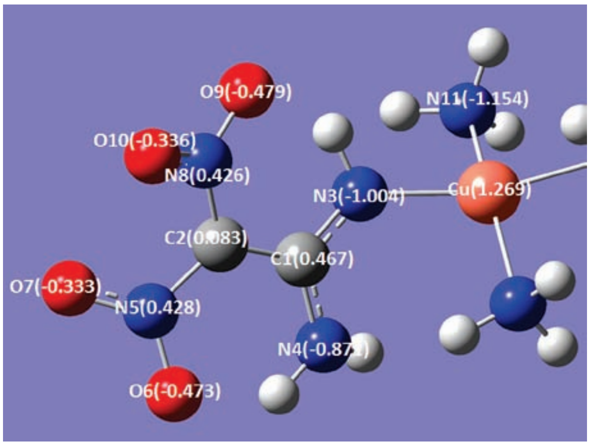

Figure 5. Calculated structure and net charges of **2** based on DFT calculations using basis MPW1PW91/SDD. One FOX ligand omitted for the clarity of the picture.

A careful comparison of the molecular conformation of **2** as predicted by density functional theory (DFT) calculations and X-ray studies show close agreement between the two. The biggest difference in the geometrically optimized bond length is for the Cu−N3 bond of **2** [1.868 (B3LYP/3-21G) Å and 1.932 (MPW1PW91/SDD) Å][19] which are slightly shorter than the corresponding experimental value [2.002(1) Å] (Table 1). The calculated values of the dihedral angles are also significantly different than the experimental values of **2**.

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Table 1. Selected Bond Lengths (Å), Bond Angles, and Dihedral Angles (deg) Determined by X-ray Diffraction and DFT Calculations of **2**

	X-ray	DFT(B3LYP/3-21G)	DFT(MPW1PW91/SDD)
		Bond Length	
Cu−N3	2.002	1.868	1.932
Cu−N11	2.013	1.958	2.074
C1−C2	1.490	1.444	1.448
C1−N3	1.286	1.324	1.336
C1−N4	1.321	1.386	1.372
C2−N5	1.355	1.420	1.427
C2−N8	1.405	1.420	1.425
N5−O6	1.266	1.329	1.299
N5−O7	1.260	1.277	1.264
N8−O9	1.233	1.331	1.301
N8−O10	1.236	1.276	1.264
		Bond Angles	
N3−Cu−N11	89.7	96.2	90.2
C2−C1−N3	120.9	123.2	122.9
C2−C1−N4	116.2	118.3	118.9
N3−C1−N4	122.8	118.5	118.1
C1−C2−N5	117.2	122.2	122.4
C1−C2−N8	120.7	120.4	121.1
N5−C2−N8	122.1	117.4	116.5
Cu−N3−C1	131.4	132.1	132.6
C2−N5−O6	117.0	119.3	118.1
C2−N5−O7	124.0	119.9	120.5
O6−N5−O7	119.0	120.8	121.4
		Dihedral Angles	
N11−Cu−N3−C1	123.0	139.9	136.3
N3−C1−C2−N5	−68.9	172.2	168.2
C2−C1−N3−Cu	146.8	143.4	152.2
C1−C2−N5−O6	−5.9	16.2	23.5
N8−C2−N5−O6	174.3	−164.0	−156.8
C1−C2−N8−O9	−1.5	14.0	22.5
C1−C2−N8−O10	177.0	−164.3	−154.9
N5−C2−N8−O9	178.3	−165.7	−157.1
N5−C2−N8−O10	−3.3	15.9	25.4

The difference between the calculated and experimental values can be attributed to the fact that the strong intermolecular interactions are absent in the gas phase structure from the calculation when compared to solid state from X-ray analysis. With the exception of charge density on Cu atom, the computed charge distribution values using two functional (B3LYP and MPW1PW91) are similar to each other (see Supporting Information). A high concentration of positive charge on the C1 carbon rather than the C2 carbon indicates the polarization of the double bond which supports the single bond nature of C1−C2 bond (1.49 Å) in the X-ray analysis. The symmetric charge distribution on N3 and N4 nitrogen atoms supports delocalization of charge between the amino groups.

Conclusion

In summary, it was possible to synthesize and determine crystal structures of **2** and **4**, first examples of copper complexes of FOX-7. The crystal structure of anhydrous K-FOX was analyzed. With the exception of $Cu(NH_3)_2(FOX)_2$ (**2**), compounds **3**−**5** can be readily obtained from the reaction of K-FOX or G-FOX with aqueous copper nitrate solution in the respective amine solutions. Compounds **3**−**5** show low impact sensitivity (12−15J) relative to compound **2** (5J). Except for compound **4** (T_d = 128.6 °C), all the other compounds **2**, **3**, and **5** are thermally (T_d = 163 °C) and hydrolytically stable. The structure of **2** was further studied using NBO calculations.

Experimental Section

DSC measurements were recorded on a TA Q10 instrument over the range of 40 to 400 at 10 °C/min. IR spectra were determined with KBr pellets for solids by using a BIORAD model 3000 FTS spectrometer. Elemental analyses data were obtained on an Exeter CE440 elemental analyzer. Guanidine-FOX was prepared according to the literature.[10]

X-ray Crystallography. A yellow plate (**1**) of dimensions 0.41 × 0.08 × 0.03 mm^2, irregular purple crystal (**2**) of dimensions 0.22 × 0.14 × 0.06 mm^2, or a thick green plate (**3**) of dimensions 0.56 × 0.20 × 0.07 mm^2 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 100(2) K during data collection.

Data collection was performed, and the unit cell was initially refined using APEX2 [v2009.3-0].[20] Data Reduction was performed using SAINT [v7.60A][21] and XPREP [v2008/2].[22] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[23] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[24] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic

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(20) *APEX2*, v2009.3-0; Bruker AXS Inc.: Madison, WI, 2009.
(21) *SAINT*, v7.60A; Bruker AXS Inc.: Madison, WI, 2009.
(22) *XPREP*, v2008/2; Bruker AXS Inc.: Madison, WI, 2008.
(23) *SADABS*, v2008/1; Bruker AXS Inc.: Madison, WI, 2008.
(24) *SHELXTL*, v2008/4; Bruker AXS Inc.: Madison, WI, 2008.

Table 2. Crystal Data and Structure Refinement for **1**, **2**, and **4**

	1	**2**	**4**
formula	$C_2H_3KN_4O_4$	$C_4H_{12}CuN_{10}O_8$	$C_{10}H_{26}CuN_{10}O_9$
Fw	186.18	391.78	493.95
crystal size (mm^3)	0.41 × 0.08 × 0.03	0.22 × 0.14 × 0.06	0.56 × 0.20 × 0.07
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	7.0375(8)	6.8796(7)	13.7262(9)
b (Å)	13.4273(16)	7.3038(7)	9.1110(6)
c (Å)	6.8708(8)	13.1982(13)	16.7776(11)
α (deg)	90	90	90
β (deg)	104.685(2)	95.9860(10)	96.3790(10)
γ (deg)	90	90	90
V (Å^3)	628.05(13)	659.56(11)	2085.2(2)
Z	4	2	4
D_c (g cm^{-3})	1.969	1.973	1.573
μ (mm^{-1})	0.817	1.725	1.113
T (K)	100(2)	100(2)	100(2)
$\lambda_{MoK\alpha}$ (Å)	0.71073	0.71073	0.71073
reflections collected	6447	6751	21379
data/restraints/parameters	1553/0/109	1631/0/107	5175/0/279
GOF on F^2	1.057	1.097	1.042
R_1 ($I > 2\sigma(I)$)	0.0339	0.0328	0.0482
wR_2 ($I > 2\sigma(I)$)	0.0739	0.0850	0.1113
R (all data)	0.0275	0.0279	0.0387
wR (all data)	0.0700	0.0825	0.1046
$\Delta\rho_{min}$ and $_{max}$ (e/Å^3)	0.363 and −0.330	0.377 and −0.367	0.554 and −0.454

thermal parameters for all non-H atoms. The H atoms were included using a riding model. One of the propyl groups in **4** is disordered over two positions. It was successfully modeled and had the relative ratio of 52:48. Details of the data collection and refinement are given in Table 2.

Synthesis of K-FOX[10] (1). To an aqueous solution of FOX-7 (0.148 g, 1 mmol in 5 mL of water), KOH solution (0.244 g, 2 mmol in 2 mL of water) was added dropwise over a period of 10−15 min. When excess methanol (50−60 mL) was added to the clear solution, pale yellow crystals precipitated and were identified as **1** (Yield 87%, 0.161 g). T_{dec} 226.7 °C; IR (KBr): $\tilde{\nu}$ = 462, 576, 638, 665, 750, 834, 1026, 1102, 1125, 1208, 1255, 1346, 1492, 1637, 3310, 3360, 3425, 3475 cm^{-1}.

Synthesis of $Cu(NH_3)_2(FOX)_2$ (2). K-FOX (0.372 g, 2 mmol) and $Cu(NO_3)_2\cdot2.5H_2O$ (0.232 g, 1 mmol in 1 mL water) were stirred in aqueous ammonia (14.8 M) solution (50 mL) for 15 min to give a clear solution at room temperature. Gradually purple crystals appeared and were identified as **2**. (Yield 63%, 0.246 g). T_{dec} 166.8 °C IR (KBr): $\tilde{\nu}$ = 418, 451, 547, 625, 691, 752, 769, 802, 835,1105, 1143, 1221, 1246, 1286, 1324, 1459, 1506, 1604, 1663, 2924, 3217,3290, 3336, 3383, cm^{-1}; Anal. Calcd. for $C_4H_{12}CuN_{10}O_8$ (391.75): C, 12.26; H, 3.09; N, 35.75; Found: C, 12.32; H, 3.10; N, 36.35.

Synthesis of $Cu(CH_3NH_2)_2(FOX)_2$ (3). Procedure same as for **2** except G-FOX (0.414 g, 2 mmol) can also be used to react with $CuNO_3\cdot2.5H_2O$ (0.232 g, 1 mmol) rather than K-FOX in 40 wt % solution of methylamine in water (5−7 mL) as the reaction medium. A brown solid precipitated from the reaction mixture and was identified as **3** (Yield 71%, 0.298 g). T_{dec} 163.2 °C; IR (KBr): $\tilde{\nu}$ = 422, 447, 563, 613, 663, 696, 754, 777, 823, 1006, 1034, 1116, 1226, 1290, 1361, 1454, 1487, 1580, 1613,1649, 2959, 3007, 3232, 3323, 3344, 3387 cm^{-1} ; Anal. Calcd. for $C_6H_{16}CuN_{10}O_8$ (419.80): C, 17.17; H, 3.84; N, 33.37; Found: C, 17.31; H, 3.81; N, 34.36.

Synthesis of $Cu(C_3H_7NH_2)_2(FOX)_2\cdot H_2O$ (4). Procedure same as for **3** except propyl amine (40% solution in water) was used as the reaction medium. After stirring for 5−10 min a green solid precipitate was obtained. Green crystals were obtained using a propylamine:water mixture (80:20) for crystallization and was identified as **4** (Yield 61%, 0.290 g). T_{dec} 128.6 °C; IR (KBr): $\tilde{\nu}$ = 454, 688, 752, 775, 837, 888, 964, 1006, 1133, 1246, 1344, 1473, 1496, 1601, 1647, 2878, 2936, 2964, 3324, 3400 cm^{-1} Anal. Calcd. for $C_{10}H_{24}CuN_{10}O_8\cdot H_2O$ (493.92): C, 24.32; H, 5.31; N, 28.36. Found: C, 24.13; H, 4.98; N, 28.04.

Synthesis of $Cu[(CH_3)_2NH]_2(FOX)_2$ (5). Procedure same as for **3** except dimethyl amine (40 wt % solution) was used as the reaction medium. After stirring for 5−10 min, a brown solid which was identified as **5** (Yield 67%, 0.299 g) precipitated from the reaction mixture. T_{dec} 169.9 °C; IR (KBr): $\tilde{\nu}$ = 619, 688, 752, 778, 835, 897, 1019, 1118, 1234, 1352, 1394, 1459, 496, 1613, 1646 3265, 3324, 3406, 3570 cm^{-1} Anal. Calcd. for $C_8H_{20}CuN_{10}O_8$ (447.85): C, 21.45; H, 4.50; N, 31.28 Found: C, 21.27; H, 4.27; N, 30.92.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **2**, and **4**. NBO data. Selected bond-lengths, bond angles, and dihedral angles of **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.