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1,1-Diamino-2,2-dintroethene (FOX-7) in Copper and Nickel Diamine Complexes and Copper FOX-7

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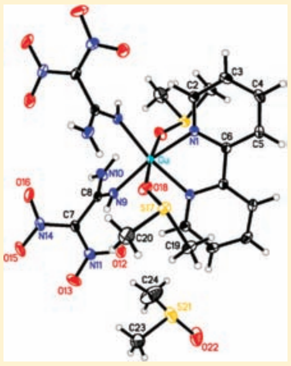
Supporting Information

ABSTRACT: 1,1-Diamino-2,2-dinitroethene (FOX-7) reacts readily with copper nitrate in an aqueous solution of potassium hydroxide to form pea green $Cu(FOX)_2(H_2O)_2$ (**5**). FOX-7 complexes of copper and nickel supported by a variety of diamines including $Cu(en)_2(FOX)_2(H_2O)$ (**1**), $Cu(pn)_2(FOX)_2$ (**2**), $Cu(bipy)(FOX)_2(H_2O)_4$ (**3a**), $Cu(bipy)_2(FOX)_2(H_2O)_{2.5}$ (**3b**), $Cu(bipy)(FOX)_2(DMSO)_2 \cdot 2DMSO$ (**3c**), $Cu(phen)_3(FOX)_2(H_2O)_3$ (**4**), $(Ni)_2(phen)_6(FOX)_4(NO_3)_3(H_2O)_2$ (**6**), and $Ni(bipy)_3(FOX)_2(H_2O)_4$ (**7a**) were obtained via metathesis reactions with potassium-FOX (K-FOX). Surprisingly FOX-7, in the presence of Ni(II) and bipyridyl in a mixed solvent of methanol and dimethyl sulfoxide, gave a chelated FOX carbamate anion resulting in the compound $Ni(bipy)_2(FOX{-}CO_2) \cdot (DMSO)$ (**7b**). All metal salts were characterized by infrared, elemental analysis, and differential scanning calorimetry (DSC). Single-crystal X-ray diffraction structures were obtained for compounds **1**, **2**, **3c**, **6**, and **7b**.



INTRODUCTION

Since the discovery of 1,1-diamino-2,2-dinitroethene (FOX-7) in 1998,[1] a considerable amount of attention has been directed toward this energetic compound as it was suggested as a potential replacement for the currently used secondary explosive cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) due to its higher threshold toward impact and friction sensitivity.[1−5] The unique structure of FOX-7, which has two electron-withdrawing nitro groups on the C1 carbon and two electron-donating amino groups on the C2 carbon, displays a "push−pull" alkene system,[1] giving rise to a fundamental chemistry of considerable interest.

Although the chemistry of FOX-7 is challenging, a wide scope of chemistry has been reported including alkylation, acylation, acetylation, halogenation, and nitration reactions.[1] However, the metal chemistry of FOX-7 has been less well studied.[6,7] The only reported metal compound of FOX-7 was its potassium salt,[6,8] K-FOX, until our recent work where we prepared the silver salt and silver and copper FOX-7 metal complexes stabilized with simple amines as ligands.[6,7] Investigation of the metal chemistry of FOX-7 highlights its characteristics as a possible ligand or an anionic species. The earlier metal complexes were shown to be thermally stable and insensitive to impact.[6,7] However, it is interesting to learn what roles FOX-7 might assume when competing with bidentate ligands to form coordination complexes with metals such as copper and nickel. Given its unique structure, FOX-7 does exhibit a variety of behaviors with metals in changing environments. More often than not, FOX-7 behaves in unpredictable ways including not reacting at all. Here, we report new chemistry of FOX-7 including the binary copper FOX-7 salt as well as additional copper and the first nickel complexes where bidentate ligands are utilized to stabilize the structure.

RESULTS AND DISCUSSION

The syntheses of copper−FOX-7 complexes with various bidentate amines were accomplished by addition of K-FOX to a solution of copper(II) nitrate in an aqueous solution of the selected diamine (Scheme 1). Purple metallic crystals [ethylenediamine (en) and 1,3-propylenediamine (pn)] and green solids [bipyridyl (bipy) and phenanthroline (phen)] precipitated from aqueous solution. The purple crystals of copper FOX-7 ethylene diamine (**1**) and 1,3-propylenediamine (**2**) complexes were obtained by allowing the solutions to evaporate slowly after all reactants were dissolved. This resulted in formation of finely divided purple solids from which larger, better-formed crystals were obtained by allowing the solids to stand in the supernatant liquid. The same procedure was followed for the nickel complexes to give orange microcrystals. Compound **1** was obtained in comparable yield by substituting FOX-7 for K-FOX. It is likely that similar results would be the case for all compounds, but these reactions were not attempted. With the exception of reactions with bipyridyl and phenanthroline that were run at 90 °C, all reactions were carried out at 25 °C.

Single-crystal X-ray diffraction structures for the copper FOX-7 complexes (**1**, **2**, and **3c**) were obtained (Figures 1, 2, and 3, respectively). Crystallographic data are summarized in Table 1 (Experimental Section). Compound **1** crystallizes in the monoclinic crystal system (space group $P2_1/c$) with four

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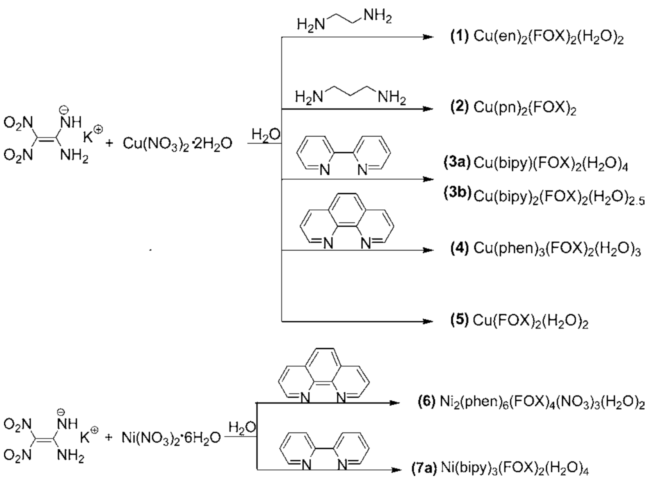
Scheme 1. Synthesis of Copper and Nickel Complexes with K-FOX and Various Diamines



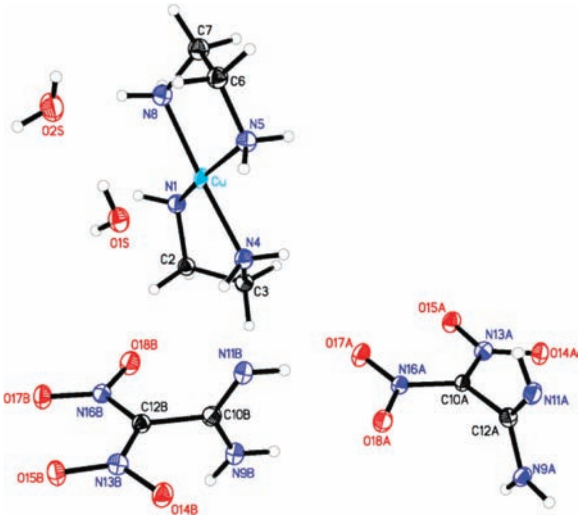


Figure 1. Thermal ellipsoid plot (30%) and labeling scheme for $Cu(en)_2(FOX)_2(H_2O)_2$ (**1**). Selected distances [Angstroms] and angles [degrees]: C(10B)−N(11B), 1.292(7); N(9B)−C(10B), 1.340(7); Cu−N(1), 2.004(5); Cu−N(8), 2.023(5); C(7)−N(8), 1.486(7); N(5)−C(6), 1.487(7); Cu−O(1S), 2.328(4); N(1)−Cu−N(4), 84.67(19); N(5)−Cu−N(8), 84.53(19); N(1)−Cu−N(8), 95.05(19); N(4)−Cu−N(5), 94.98(19); N(1)−Cu−N(5), 166.28(19); N(1)−Cu−O(1S), 99.99(17); N(5)−Cu−O(1S), 93.73(17).

molecules per unit cell (Figure 1). The two ethylenediamine ligands surround the central copper(II) atom with one water molecule and one FOX molecule at a longer distance (viz., Cu−N (en) × 4, 2.023 Å; Cu−O (water), 2.328 Å; Cu−O (FOX), 3.045 Å) to give a six-coordinate octahedral coordination sphere (Figure 1). The N(1)−Cu−N(4) angle is 84.67°, which is somewhat smaller compared with the value for the N(1)−Cu−N(2) angle of 86.2° for $Cu(en)_2(NO_3)_2$.[7] The loss of a proton by FOX-7 to form the FOX-7 anion is supported by the fact that the C−NH bond is shorter than the $C-NH_2$ bond by 0.05 Å, which is good agreement with the values observed for monoamine complexes, $Cu(NH_3)_2(FOX)_2$ and $Cu(C_3H_7NH_2)_2(FOX)_2$.[7]

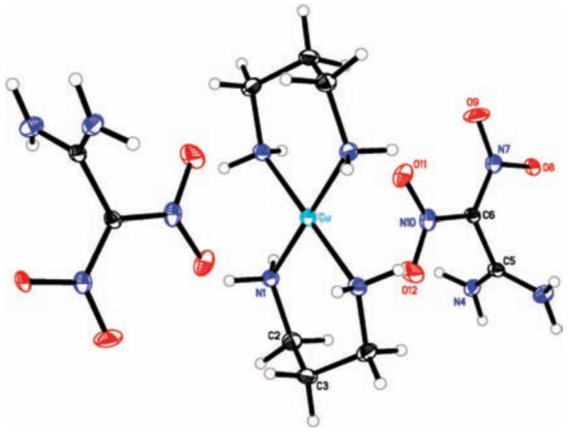


Figure 2. Thermal ellipsoid plot (30%) and labeling scheme for $Cu(pn)_2(FOX)_2$ (**2**). Selected distances [Angstroms] and angles [degrees]: Cu−N(1)#1 = Cu−N(1)#2 = Cu−N(1)#3 = Cu−N(1)#4, 2.024(2); N(4)−H(4B) = 0.906(19); N(4)−H(4A) = 0.901(18); N(1)#1−Cu−N(1)#2, 86.70(14); N(1)#1−Cu−N(1)#3, 93.30(14); N(1)#2−Cu−N(1)#3, 180.0; N(1)#1−Cu−N(1), 180.0.

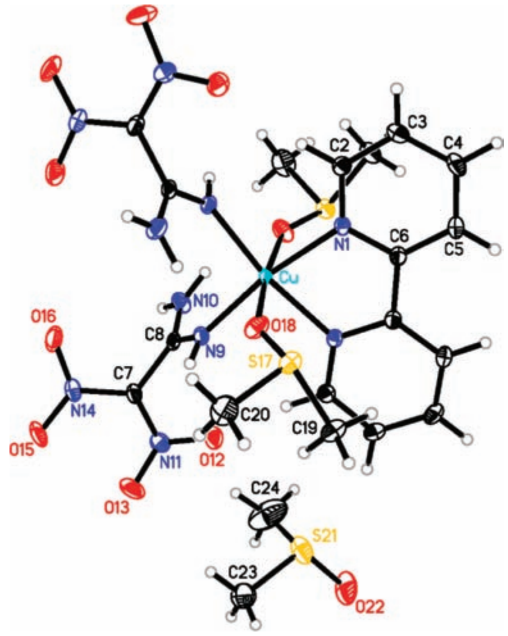


Figure 3. Thermal ellipsoid plot (30%) and labeling scheme for $Cu(bipy)(FOX)_2(DMSO)_2{\cdot}2DMSO$ (**3c**). Selected distances [Angstroms] and angles [degrees]: Cu−N(9), 1.9767(15); Cu−N(1), 2.0412(16); Cu−O(18)#1, 2.4270(14); C(8)−N(9), 1.299(2); C(8)−N(10), 1.330(2); N(9)−Cu−N(9)#1, 96.25(9); N(9)#1−Cu−N(1), 92.31(6); N(9)#1−Cu−N(1)#1, 170.34; N(9)−Cu−O(18)#1, 98.74(6); N(1)−Cu−O(18)#1, 86.47(5); N(1)−Cu−N(1)#1, 79.53(9); S(17)−O(18)−Cu, 148.99(9); C(20)−S(17)−C(19), 97.82(11).

Compound **2** also crystallizes in a monoclinic crystal system (space group *C*2/*m*) with two molecules per unit cell (Figure 2). The two propylenediamine ligands coordinate to the central copper(II) atom with a concomitant interaction via the oxygen of the nitro group of FOX giving a six-coordinate octahedral coordination sphere, viz., Cu−N (pn) × 4, 2.023 Å; Cu−O (FOX) × 2, 2.798 Å.

The crystal structure of the FOX-7 moiety appears as if it has four protons; however, each FOX-7 anion has a charge of minus one with only three protons per moiety. This occurs because the hydrogen on N4 occupies each position only one-half of the time (Figure 2). The system is highly hydrogen bonded between the N−H of the pn ligand which is

Table 1. Crystal Data and Structure Refinement for 1, 2, 3c, 6, and 7b

	1	2	3c	6	7b
formula	$C_8H_{26}CuN_{12}O_{10}$	$C_{10}H_{26}CuN_{12}O_8$	$C_{22}H_{38}$ $CuN_{10}O_{12}S_4$	$C_{80}H_{68.40}N_{31}Ni_2O_{27.70}$	$C_{25}H_{24}N_8NiO_7S$
fw	513.95	505.97	826.4	2024.68	639.27
cryst size (mm^3)	0.17 × 0.12 × 0.01	0.40 × 0.28 × 0.04	0.43 × 0.29 × 0.17	0.23 × 0.11 × 0.05	0.11 × 0.10 × 0.02
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$C2/m$	$C2/c$	P-1	$P2_1/n$
a (Å)	13.363(5)	17.461(3)	24.377(3)	9.9134(17)	11.195(3)
b (Å)	11.495(4)	6.7620(10)	11.7645(12)	14.553(2)	15.925(4)
c (Å)	12.708(5)	9.8590(10)	17.213(2)	16.056(3)	15.613(4)
α (deg)	90	90	90	66.395(2)	90
β (deg)	97.329(5)	123.609(10)	134.042(3)	84.118(2)	103.266(3)
γ (deg)	90	90	90	81.961(2)	90
V ($Å^3$)	1936.0(12)	969.5(2)	3548.4(7)	2099.0(6)	2709.2(10)
Z	4	2	4	1	4
D_c (g cm^{-3})	1.763	1.733	1.501	1.602	1.567
μ (mm^{-1})	1.208	1.198	0.921	0.553	0.855
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
$\lambda_{\mathrm{Mo\ K\alpha}}$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
reflns collected	15303	4057	15821	19392	23837
data/restraints/params	3558/194/298	978/2/92	3651/12/226	8633/74/683	5546/0/380
GOF on F^2	0.994	1.033	1.125	1.035	1.012
R_1 ($I > 2\sigma(I)$)	0.0598	0.039	0.0293	0.0473	0.0545
wR_2 ($I > 2\sigma(I)$)	0.1361	0.0762	0.0722	0.1217	0.1164
R (all data)	0.1058	0.0577	0.0338	0.057	0.1061
wR (all data)	0.1592	0.0825	0.0745	0.1291	0.1375
$\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ (e/$Å^3$)	0.596 and −1.053	0.389 and −0.528	0.761 and −0.659	2.549 and −1.066	1.024 and −0.912

coordinated to copper and the oxygen atom of the nitro group of FOX-7.

Recrystallization of **3a**, **3b**, and **4** was very difficult due to solubility problems. Green crystals of the **3b** and **4** complexes were obtained by recrystallizing each from water. However, the crystals were not suitable for X-ray analysis. When the crystals remained in aqueous solution for an extended period, the complexes underwent slow hydrolysis resulting in formation of crystals of yellow FOX-7. This observation was also made in earlier attempts to characterize copper FOX-7 monodentate amine complexes.[7]

Suitable crystals of $Cu(bipy)(FOX)_2(DMSO)_2 \cdot 2DMSO$ (**3c**) were obtained by vapor diffusion of methanol into a solution of **3b** in DMSO to give dark green crystals. Prior to recrystallization, elemental analysis data supported the product, **3b**, consisting of one copper atom with two bipyridyl ligands and two FOX anions with 2.5 water molecules of crystallization (Scheme 1). After recrystallization from methanol and DMSO, one of the bipyridyl ligands had been displaced by two DMSO molecules.[9] X-ray analysis and elemental analysis indicated the presence of a single bipyridyl ligand, two FOX ligands, and two DMSO moieties, **3c** (Scheme 2).

Scheme 2. Recrystallization of $Cu(bipy)_2(FOX)_2$ (3b) from DMSO/MeOH To Form $Cu(bipy)(FOX)_2(DMSO)_2 \cdot 2DMSO$ (3c)

$$Cu(bipy)_2(FOX)_2(H_2O)_{2.5}\ (\mathbf{3b}) \xrightarrow[\text{RT}]{\text{DMSO/MeOH}} Cu(bipy)(FOX)_2(DMSO)_2 \cdot 2(DMSO)\ (\mathbf{3c})$$

Compound **3c** crystallizes in a monoclinic space group $C2/c$ with four molecules in the unit cell (Figure 3). The distorted octahedral complex consists of a copper atom bonded to two FOX-7 anions, two molecules of DMSO, one bipy ligand, and two DMSO molecules of solvation with bond distances Cu−N (bipy) × 2, 2.041 Å; Cu−O (DMSO) × 2, 2.427 Å; Cu−N (FOX) × 2, 1.977 Å.

Because one of the bipy ligands had been displaced from **3b** by two DMSO ligands, the complex consists of a metal environment which is similar to the monodentate cases described in our previous work.[7] The N(9)−Cu bond is shorter than the N(1)−Cu bond, which suggests that FOX is more tightly bonded to the Cu core than is the bipyridyl ligand. It is seen that C(8)−N(9) < C(8)−N10 in the FOX structure, supporting loss of a proton and formation of FOX as an anion, which was observed in structures of **1**, **2**, **3c**, **6**, and **7b.**

The only metal compound of FOX-7 was its potassium salt, K-FOX, until our recent work where we prepared the silver salt and silver and copper FOX-7 metal complexes stabilized with simple amine as ligands.[6,7] We now report the essentially quantitative precipitation of $Cu(FOX)_2(H_2O)_2$ (**5**), which was isolable as a stable pea green powder from a room temperature metathetical reaction of K-FOX in an aqueous solution of copper(II) nitrate.[6] The $Cu(FOX)_2(H_2O)_2$ salt is thermally decomposed at 171.6 °C but stable in air and supported by good elemental analysis. It is less stable thermally than FOX-7 or K-FOX but more thermally stable than the bidentate copper FOX complexes described in this work with the exception of **1**.

Single-crystal X-ray diffraction structures were obtained for nickel complexes **6** and **7b**. Compound **6** is a dimer, which crystallizes in a triclinic (P-1) crystal system with one molecule per unit system. The complex consists of three phenanthroline ligands forming an octahedral coordination sphere around each central nickel atom along with water molecules of crystallization and nitrate and FOX-7 anions (Figure 4).

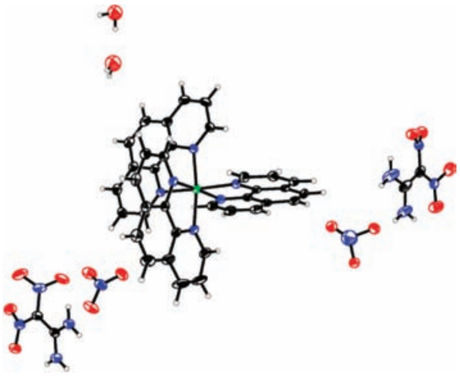


Figure 4. Thermal ellipsoid plot (30%) and labeling scheme for $(Ni)_2(phen)_6(FOX)_4(NO_3)_3(H_2O)_2$ (**6**).

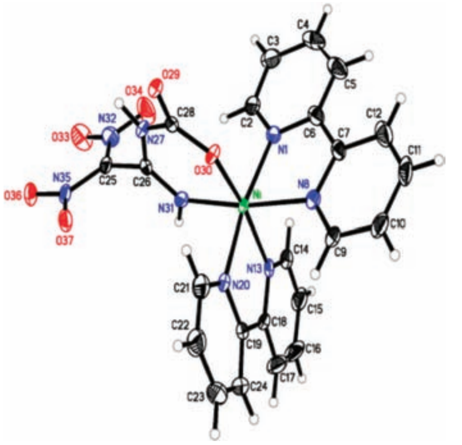


Figure 5. Thermal ellipsoid plot (30%) and labeling scheme for $Ni(bipy)_2(FOX-CO_2)\cdot(DMSO)$ (solvated DMSO not shown) **7b**. Selected distances [Angstroms] and angles [degrees]: Ni−N(31), 2.018(3); Ni−O(30), 2.037(3); Ni−N(1), 2.101(3); Ni−N(8), 2.108(3); C(28)−O(30), 1.276(4); C(28)−N(27), 1.401(5); C(26)−N(27), 1.376(5); C(26)−N(31), 1.285(5); O(30)−C(28)−N(27), 119.9(3); N(31)−Ni−O(30), 90.76(12); N(31)−Ni−N(20), 94.84(12); N(20)−Ni−N(1), 94.90(13); C(28)−Ni−O(30), 129.7(3); C(26)−N(31)−Ni, 127.5(3).

Compound **7a** exists as orange microcrystals which were too small for X-ray analysis. The compound was confirmed by elemental analysis, IR, and DSC, which supported formation of $Ni(bipy)_3(FOX)_2(H_2O)_4$. While attempting to obtain suitable crystals for X-ray analysis, recrystallization of **7a** using DMSO/MeOH in the same manner as discussed for **3c** reproducibly gave crystals which were found by X-ray analysis to be compound **7b**.

Interestingly, the crystal structure showed an unexpected transformation of the FOX-7 moiety such that addition of carbon bonded to two oxygen atoms to the amine functional group had taken place upon recrystallization in DMSO/MeOH. The complex crystallizes in a monoclinic space group of $P2_1/n$ with 4 molecules per unit cell. The central nickel atom is in a distorted octahedral configuration coordinated to two bipy ligands and one bidentate FOX-7−CO_2 moiety in which bonding to the metal is via the nitrogen of a FOX−NH group and the oxygen of the CO_2 group (Figure 5). A molecule of DMSO is hydrogen bonded at N(31) [N(31)−H(31)···O39#2]. Bond C(26)−N(31) is 0.09 Å shorter than C(26)−N(27), displaying the effect of the electronegative oxygen on the latter bond length.

Thermal Stabilities and Impact Sensitivity. Differential scanning calorimeter (DSC) data for all compounds were obtained. The copper complexes have thermal stabilities of 178.0 (**1**), 161.2 (**2**), 153.2 (**3a**), 156.4 (**3b**), 167.2 (**3c**), 169.5 (**4**), and 171.6 °C (**5**) . The nickel complexes decompose at 193.3 (**6**), 197.4 (**7a**), and 225.5 °C (**7b**). In general, the nickel complexes are thermally more stable than the analogous copper complexes. All decompose without explosion. Not unexpectedly, the impact sensitivities for all compounds which were determined with BAM Fallhammer tests[9] were found to be greater than 40 J.

CONCLUSION

Copper and nickel metal complexes of FOX-7 were synthesized with various bidentate diamine ligands in moderate yields. All compounds were characterized and analyzed via IR, elemental analysis, and differential scanning calorimetry (DSC). Single-crystal X-ray diffraction data were obtained for compounds **1**, **2**, **3c**, **6**, and **7b**. These materials show thermal stabilities between 156 and 225 °C, which is slightly less stable than FOX-7 (~261 °C) and K-FOX (226 °C).[7] The new metal complexes presented in this paper are not energetic, and as expected, they are less sensitive to impact (≥40 J) than K-FOX (33 J). In **3c** and **7b**, the only two examples where the metal forms bonds with the nitrogen atoms of both bipy and FOX, it is seen the bond length is very slightly shorter for the FOX nitrogen.

EXPERIMENTAL SECTION

Caution: Although none of the compounds described herein has exploded or detonated in the course of this research, FOX-7 is an insensitive munition, and all of these materials should be handled with extreme care using proper safety practices.

General Methods. IR spectra were recorded as KBr pellets using a BIORAD model 3000 FTS spectrometer. DSC measurements were performed on a TA Q10 instrument over the range from 40 to 400 °C at a heating rate of 5 °C/min. Elemental analyses were performed on an Exeter CE440 element analyzer. Occasionally the agreement between experimental and theoretical values for carbon and hydrogen is outside of the acceptable range; this arises most usually for hydrated species. The values obtained for nitrogen often are a function of the nitrogen percentage in the compound; a lower nitrogen content most frequently results in better agreement. K-FOX was prepared by reaction of FOX-7 with potassium hydroxide in water.[7,8] All other reagents were used as purchased and of reagent grade.

X-ray Crystallography. A purple plate (**1**) of dimensions 0.17 × 0.12 × 0.01 mm^3, a purple plate (**2**) of dimensions 0.40 × 0.28 × 0.04 mm^3, an irregular green crystal (**3c**) of dimensions 0.43 × 0.29 × 0.17 mm^3, a thin gold plate (**6**) of dimensions 0.29 × 0.19 × 0.04 mm^3, or an orange plate (**7b**) of dimensions 0.11 × 0.10 × 0.02 mm^3 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. Crystals were irradiated using graphite monochromated Mo Kα radiation (λ = 0.71073). An Oxford Cobra low-temperature device was used to maintain 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].[10]Data reduction was performed using SAINT [v7.60A][11]and XPREP [v2008/2].[12] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[13] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[14] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. Details of the data collection and refinement are given in Table 1.

$Cu(NH_2CH_2CH_2NH_2)_2(FOX)_2 \cdot 2H_2O$ (1). A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.232 g, 1.0 mmol in 3 mL of water) was added dropwise to a solution of ethylenediamine (78 mmol, 4.68 g in 3 mL of water) followed by addition of powdered K-FOX (0.374 g, 2 mmol) with stirring at 25 °C. After 5−10 min, a purple precipitate formed. It was removed by filtration and dried under vacuum (0.250 g, yield 49%). Purple crystals were formed by maintaining the unfiltered solution at 90 °C for 15 min and then allowing the solution to stand overnight. T_{dec} 178.6 °C. IR (KBr): ν = 3437, 3327, 3290, 3263, 2956, 2723, 2482, 2194, 1635, 1575, 1500, 1444, 1347, 1281, 1245, 1141, 1114, 1042, 893, 830, 745, 687, 663 cm^{-1}. Anal. Calcd for $C_8H_{26}CuN_{12}O_{10}$ (513.95); C, 18.70; H, 5.10; N, 32.17. Found: C, 18.71; H, 5.11; N, 32.44.

$Cu(NH_2CH_2CH_2CH_2NH_2)_2(FOX)_2$ (2). A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.232 g, 1.0 mmol in 3 mL of water) was added dropwise to a solution of 1,3-propylenediamine (78 mmol, 5.78 g in 3 mL of water) followed by addition of K-FOX (0.374 g, 2 mmol) as a solid powder. The reaction was stirred at room temperature. Within 5−10 min of stirring, a purple precipitate formed. The precipitate was filtered and dried under vacuum. Purple crystals of the product were formed by heating the unfiltered solution at 90 °C for 15 min and then allowing the solution to remain overnight (0.347 g, yield 69%). T_{dec} 161.2 °C. IR (KBr): ν = 3048, 3296, 3241, 3136, 3042, 2980, 2932, 2889, 2824, 2341, 1659, 1610, 1493, 1415, 1386, 1343, 1281, 1220, 1178, 1132, 1065, 1029, 923, 876, 830, 794, 743, 680 cm^{-1}. Anal. Calcd for $C_{10}H_{26}CuN_{12}O_8$ (505.97): C, 23.74; H, 5.18; N, 33.22. Found: C, 23.79; H, 5.21; N, 32.66.

$Cu(bipy)(FOX)_2(H_2O)_4$ (3a). 2,2′-Bipyridyl (0.5 mmol, 0.078 g) was added to a solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.116 g, 0.5 mmol in 5 mL of water) and stirred until all the bipy dissolved. To the solution, K-FOX (0.093 g, 0.5 mmol) was then added as a powder. The reaction formed a precipitate almost immediately to give a turquoise green solid which was stirred for ∼30 min, and the precipitate was filtered and dried under vacuum (0.225 g, yield 77%). T_{dec} 153.2 °C. IR (KBr): ν = 3417, 3328, 3300, 1619, 1500, 1473, 1448, 1385, 1325, 1218, 1193, 1161, 1138, 1070, 1019, 860, 829, 789, 771, 755, 731, 625 cm^{-1}. Anal. Calcd for $C_{14}H_{22}CuN_{10}O_{12}$ (585.93): C, 28.70; H, 3.78; N, 23.91. Found: C, 28.88; H, 3.11; N, 22.96.

$Cu(bipy)_2(FOX)_2(H_2O)_{2.5}$ (3b). 2,2′-Bipyridyl (0.234 g, 1.5 mmol) was added to a solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.116 g, 0.5 mmol in 5 mL of water) and stirred until all the bipy was dissolved. To the solution, powdered K-FOX (0.187 g, 1 mmol) was then added. The reaction formed a clear green solution which was stirred for an additional 30 min. The solvent was then removed by blowing air over the surface to give a sticky substance. This was then triturated with ∼5 mL of acetonitrile to give a light green solid, which was removed by filtration and air dried (0.220 g, yield 62%). T_{dec} 156.4 °C. IR (KBr): ν = 3424, 3401, 3329, 3296, 1626, 1600, 1518, 1505, 1474, 1389, 1331, 1194, 1163, 1138, 1064, 1018, 860, 793, 754, 622 cm^{-1}. Anal. Calcd for $C_{24}H_{27}CuN_{12}O_{10.5}$ (715.09): C, 40.31; H, 3.81; N, 23.50. Found: C, 40.54; H, 3.11; N, 22.91.

$Cu(bipy)(FOX)_2(DMSO)_2 \cdot 2$ DMSO (3c). Compound **3c** was obtained by dissolving a minimum amount of **3b** in DMSO and placing it inside of a chamber which contained methanol to give crystals of **3c** slowly. T_{dec} 167.2 °C. IR (KBr): ν = 3373, 3242, 3118, 3064, 2766, 2363, 2025, 1644, 1605, 1569, 1529, 1499, 1477, 1446, 1357, 1328, 1294, 1274, 1174, 1153, 1143, 1099, 1061, 1034, 858, 828, 773, 731, 639 cm^{-1}.

$Cu(phen)_3(FOX)_2(H_2O)_3$ (4). 1,10-Phenanthroline monohydrate (1.5 mmol, 0.297 g) was added to a solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.116 g, 0.5 mmol in 3 mL of water) and placed into an oil bath at 85−90 °C until the phenanthroline dissolved. Powdered K-FOX (0.187 g, 1 mmol) was then added to the solution and stirred for ∼30 min in the oil bath. The turquoise precipitate was filtered and dried under vacuum (0.280 g, yield 59%). T_{dec} 169.5 °C. IR (KBr): ν = 3431, 3390, 3213, 3065, 2364, 2343, 1638, 1601, 1541, 1518, 1473, 1429, 1385, 1363, 1343, 1239, 1130, 1036, 1004, 952, 909, 869, 776, 766, 754, 723, 644, 629 cm^{-1}. Anal. Calcd for $C_{40}H_{36}CuN_{14}O_{11}$ (952.35): C, 50.45; H, 3.81; N, 20.59. Found: C, 50.15; H, 3.54; N, 19.72.

$Cu(FOX)_2(H_2O)_2$ (5). To a suspension of FOX-7 (1 mmol, 0.148 g) in 0.8 mL of water, a solution of potassium hydroxide, KOH (0.14 mL of 11.11 M), was added dropwise to give a clear dark yellow solution. An aqueous solution of copper(II) nitrate (0.5 mmol, 0.116 g in 0.5 mL) was then added dropwise. With the first drop, a pea green precipitate formed immediately. After addition is complete, the reaction was stirred for 24 h, filtered, and washed with a small amount of water (0.207 g, yield ∼99%). T_{dec} 171.6 °C. IR (KBr): 3569, 3423, 3405, 3331, 3298, 3227, 2923, 2475, 2361, 2243, 1933, 1633, 1518, 1473, 1394, 1353, 1221, 1166, 1139, 1025, 859, 791, 752, 673, 622 cm^{-1}. Anal. Calcd for $C_4H_{10}CuN_8O_{10}$ (393.72): C, 12.20; H, 2.56; N, 28.46. Found: C, 12.01; H, 2.25; N, 26.03.

$(Ni)_2(phen)_6(FOX)_4(NO_3)_3(H_2O)_2$ (6). 1,10-Phenanthroline monohydrate (1.5 mmol, 0.297 g) was added to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.5 mmol in 3 mL of water) and heated at 85−90 °C. Powdered K-FOX (0.187 g, 1 mmol) was added, and the mixture was stirred for 15 min. The solution was cooled slowly to 25 °C and orange crystals formed. They were filtered and dried under vacuum (0.390 g, yield 77%). T_{dec} 193.3 °C. IR (KBr): ν = 3396, 3058, 2931, 2461, 2292, 1982, 1625, 1583, 1517, 1491, 1423, 1384, 1337, 1317, 1237, 1132, 1101, 887, 849, 778, 748, 725, 669, 642 cm^{-1}. Anal. Calcd for $C_{80}H_{68.40}N_{31}Ni_2O_{27.70}$ (2024.68): C, 47.46; H, 3.41; N, 21.45. Found: C, 47.34; H, 3.43; N, 20.57.

$Ni(bipy)_3(FOX)_2(H_2O)_4$ (7a). 2,2′-Bipyridyl (1.5 mmol, 0.234 g) was added to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.5 mmol in 3 mL of water) and placed into an oil bath at 85−90 °C to give a clear red solution. Powdered K-FOX (0.187 g, 1 mmol) was added, and the solution was stirred for 15 min in the oil bath. The solution was cooled slowly to 25 °C in which orange microcrystals formed overnight. The crystals were filtered and dried under vacuum (0.429 g, yield 96%). T_{dec} 197.4 °C. IR (KBr): ν = 3421, 3108, 3078, 2366, 2150, 1637, 1598, 1567, 1522, 1473, 1440, 1381, 1353, 1313, 1236, 1128, 1018, 908, 830, 777, 737, 650 cm^{-1}. Anal. Calcd for $C_{34}H_{38}N_{14}NiO_{12}$ (893.45): C, 45.71; H, 4.29; N, 21.95. Found: C, 45.49; H, 3.67; N, 21.56.

$Ni(bipy)_2(FOX\text{-}CO_2) \cdot (DMSO)$ (7b). In a 4 mL vial, 0.102 g of **7a** was dissolved in 0.5 mL of DMSO and placed into a chamber of methanol (2.5 mL) in which orange crystals formed. They were filtered and air dried to give **7b**. T_{dec} 225.5 °C. IR (KBr): 3650, 3512, 3424, 3202, 3109, 3078, 2993, 2905, 1642, 1602, 1573, 1479, 1443, 1359, 1311, 1240, 1172, 1136, 1043, 1020, 970, 894, 803, 766, 737, 711, 651, 631 cm^{-1}. Anal. Calcd for $C_{25}H_{24}N_8NiO_7S$ (639.27): C, 46.97; H, 3.78; N, 17.53. Found: C, 46.49; H, 3.70; N, 17.96.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for **1**, **2**, **3c**, **6**, and **7b**; selected bond lengths, bond angles, and dihedral angles and ball and stick packing diagram of **1**, **2**, **3c**, **6**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) www.bam.de. (b) A 15−20 mg portion of the copper or nickel complex of FOX-7 was subjected to a Bam Fallhammer test using a 10 kg weight: insensitive > 40 J; less sensitive ≥ 35 J; sensitive ≥ 4 J.; very sensitive ≤ 3J.

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