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

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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(H2O)2 (5). FOX-7 complexes of copper and nickel supported by a variety of diamines including Cu-(en)2(FOX)2(H2O) (1), Cu(pn)2(FOX)2 (2), Cu(bipy)(FOX)2(H2O)4 (3a), Cu(bipy)2(FOX)2(H2O)2.5 (3b), Cu(bipy)(FOX)(DMSO)2.DMSO (3c), Cu(phen)2(FOX2(H2O)3 (4), (Ni)2(phen)2(FOX)2(NO3)3(H2O)2 (6), and Ni(bipy)(FOX)2(H2O)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–CO2){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). 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 amine 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 [ethylendediamine (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 P21/c) with four...
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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(NO3)2.

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−NH2 bond by 0.05 Å, which is good agreement with the values observed for monoamine complexes, Cu(NH3)2(FOX)2 and Cu(C6H4NH2)2(FOX)2.

Compound 2 also crystallizes in a monoclinic crystal system (space group C2/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, 2.024(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.

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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.

Suitable crystals of Cu(bipy)(FOX)2(DMSO)2·2DMSO (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 two water molecules of crystallization (Scheme 1). After recrystallization from methanol and DMSO, one of the bipyridyl ligands had been displaced by 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, suggesting 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 copper FOX-7 metal complexes stabilized with simple amine as ligands.6,7 We now report the essentially quantitative precipitation of Cu(FOX)2(H2O)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. The Cu(FOX)2(H2O)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 copper atom.

### Scheme 2. Recrystallization of Cu(bipy)2(FOX)2 (3b) from DMSO/MeOH To Form Cu(bipy)(FOX)2(DMSO)2·2DMSO (3c)

\[
\text{Cu(bipy)}_2(FOX)_2(H_2O)_{2.5} \xrightarrow{\text{DMSO/MeOH, } RT} \text{Cu(bipy)(FOX)2(DMSO)2} \]

\[ \cdot 2(\text{DMSO}) \] (3c)
central nickel atom along with water molecules of crystallization and nitrate and FOX-7 anions (Figure 4).

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)2(FOX)2(H2O)6. 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 P21/c 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 moiety in which bonding to the metal is via the nitrogen of a FOX–NH group and the oxygen of the CO2 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 calorimetry (DSC) data for all compounds were obtained. The copper complexes have thermal stabilities of 156 and 225 °C, which is slightly less stable than FOX-7 (~261 °C) and K-FOX (226 °C). 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 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 mm3, a purple plate (2) of dimensions 0.40 × 0.28 × 0.04 mm3, an irregular green crystal (3c) of dimensions 0.43 × 0.29 × 0.17 mm3, a thin gold plate (6) of dimensions 0.29 × 0.19 × 0.04 mm3, or an orange plate (7b) of dimensions 0.11 × 0.10 × 0.02 mm3 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion oil. Data were collected on a Bruker three-circle X-ray 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
**Cu(NH$_3$)$_2$CH$_2$CH$_2$NH$_2$)$_2$(FOX)$_2$2H$_2$O (1).** A solution of Cu(NO$_3$)$_2$.2.5H$_2$O (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 powder 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 94%). Purple crystals of the product were included using a riding model. Details of the data collection and refinement are given in Table 1.

**Cu(NO$_3$)$_2$.2.5H$_2$O (3a).** A solution of Cu(NO$_3$)$_2$.2.5H$_2$O (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 at 90 °C for 15 min and then allowing the solution to stand overnight. $T_{de}$: 178.6 °C. IR (KBr): $\nu$: 3437, 3327, 3296, 3265, 2958, 2732, 2482, 1948, 1635, 1575, 1456, 1437, 1281, 1245, 1148, 1114, 1044, 893, 830, 745, 687, 663 cm$^{-1}$. Anal. Calcld for C$_{10}$H$_{26}$CuN$_{12}$O$_8$ (505.97): C, 23.74; H, 5.18; N, 33.22. Found: C, 28.88; H, 3.11; N, 26.66.

**Cu(bipy)$_2$(FOX)$_2$(H$_2$O)$_2$ (2).** A solution of Cu(NO$_3$)$_2$.2.5H$_2$O (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 at 90 °C for 15 min and then allowing the solution to stand overnight (0.347 g, yield 69%). $T_{de}$: 161.2 °C. IR (KBr): $\nu$: 3048, 3096, 3214, 3136, 3042, 2980, 2932, 2889, 2824, 2341, 1659, 1610, 1493, 1415, 1386, 1343, 1281, 1220, 1178, 1132, 1065, 1029, 923, 876, 790, 743, 680 cm$^{-1}$. Anal. Calcld for C$_{14}$H$_{22}$CuN$_{10}$O$_{12}$ (585.93): C, 28.70; H, 3.78; N, 23.91. Found: C, 28.87; H, 3.11; N, 22.96.

**Cu(bipy)$_2$(FOX)$_2$(H$_2$O)$_{2.5}$ (3b).** A 2,2'-Bipyridyl (0.05 mm, 0.078 g) was added to a solution of Cu(NO$_3$)$_2$.2.5H$_2$O (0.116 g, 0.5 mmol in 5 mL of water) and stirred until all the bipy dissolved. The solution formed a precipitate almost immediately to give a turquoise green solid which was stirred for 30 min, and the precipitate was filtered and air dried to give Cu(bipy)$_2$(FOX)$_2$(H$_2$O)$_{2.5}$ (0.116 g, 0.5 mmol in 5 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 and orange crystals formed. They were filtered and dried under vacuum (0.390 g, yield 77%). $T_{de}$: 193.3 °C. IR (KBr): $\nu$: 3336, 3058, 2931, 2461, 2292, 1982, 1625, 1583, 1517, 1491, 1423, 1384, 1337, 1317, 1332, 1101, 887, 849, 778, 748, 725, 669, 642 cm$^{-1}$. Anal. Calcld for C$_{24}$H$_{36}$CuN$_{10}$O$_{12}$ (939.45): C, 47.46; H, 3.41; N, 21.45. Found: C, 47.34; H, 3.43; N, 20.57.

**Ni(bipy)$_2$(FOX)$_2$(H$_2$O)$_2$ (7a).** A 2,2'-Bipyridyl (1.5 mmol, 0.234 g) was added to a solution of Ni(NO$_3$)$_2$.6H$_2$O (0.145 g, 0.5 mmol in 3 mL of water) and heated 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%). $T_{de}$: 197.4 °C. IR (KBr): $\nu$: 3421, 3108, 3078, 2736, 2150, 1637, 1598, 1567, 1522, 1473, 1440, 1381, 1353, 1313, 1236, 1128, 1018, 908, 877, 737, 650 cm$^{-1}$. Anal. Calcld for C$_{34}$H$_{38}$N$_{14}$NiO$_{12}$ (983.45): C, 45.71; H, 4.29; N, 21.95. Found: C, 45.49; H, 3.67; N, 21.56.

**Ni(bipy)$_2$(FOX)$_2$(DMSO)$_2$ (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. $T_{de}$: 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. Calcld for C$_{34}$H$_{38}$Ni$_2$O$_{3}$S (639.27): C, 46.97; H, 3.78; N, 17.53. Found: C, 46.49; H, 3.70; N, 17.36.

**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 ≤ 3 J.


