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Novel Luminescent Tetranuclear and Pentanuclear Copper(I)–Dithiolates

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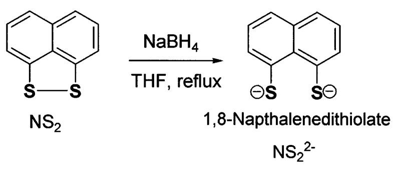
Tetranuclear $[Cu_4(\mu_2\text{-dppm})_3(\mu_2\text{-}\mu_2\text{-NS}_2)(\mu_2\text{-}\mu_4\text{-NS}_2)]$ (**1**) and pentanuclear $[Cu_5(\mu_2\text{-dppm})_4(\mu_3\text{-}\mu\text{-}_3\text{-NS}_2)_2]PF_6$ (**2**·PF_6) (dppm = bis(diphenylphoshino)methane, NS_2^{2-} = 1,8-naphthalenedithiolate) were synthesized from the reactions between NS_2^{2-} and $[Cu_2(\mu_2\text{-dppm})_2(CH_3CN)_2](PF_6)_2$. Compound **1** features a square Cu_4 core capped by a 5-coordinate S atom while **2**·PF_6 exhibits an unprecedented square planar Cu_5 core. Both complexes display dual emissions at 480 and 620 nm which arise from ligand-centered nπ* and ligand–metal charge-transfer excited states, respectively.

As an emerging class of inorganic materials,[1] polynuclear Cu^I−chalcogenide species are drawing considerable attention because of their rich photophysics, photochemistry,[2] and structural diversity.[2−5] Many novel structures have been discovered in the search for emissive Cu^I clusters as exemplified by the compound $[Cu_4(\mu_2\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$[2a,b,e] which displays an unprecedented square pyramid comprising a square Cu^I_4 core capped by a tetracoordinate S^{2-} ion. The work underscored the function of the S atom as a nucleating center for copper ions, and in fact, monothiolates,[3] 1,1-dithiolates,[4] and 1,2-dithiolates[5] have long been used in the synthesis of Cu^I aggregates of high nuclearity, many of them displaying intriguing structures such as icosahedral $[Cu_8(S_2R)_6]^{4-}$ ($R = CC(CN)_2$)[4a] and $\{Cu_9(\mu_2\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_4\}(PF_6)$.[4c] Herein we report the synthesis, structures, and spectroscopy of two novel luminescent polynuclear Cu^I complexes of 1,8-naphthalenedithiolate (NS_2^{2-}) (Scheme 1). The ligand is chosen partly because of its rather unexplored coordination chemistry, but more importantly, unlike many 1,1- and 1,2-dithiolates, 1,8-naphthalenedithiolate is unique for its rigid backbone and parallel alignment of its two C−S bonds. These features of the ligand are expected to give rise to cuprous clusters with new structures.

Scheme 1



1,8-Naphthalenedithiolate (NS_2^{2-})[6a] was prepared in situ by reducing naphtho[1,8-cd]-1,2-dithiole[6b] (NS_2) with $NaBH_4$ in refluxing THF (Scheme 1). Reacting NS_2^{2-} and 2 molar equiv of $[Cu_2(\mu_2\text{-dppm})_2(CH_3CN)_2](PF_6)_2$[7] at room temperature for 1 h gave the tetranuclear complex $[Cu_4(\mu_2\text{-dppm})_4(\mu_2\text{-}\mu_2\text{-NS}_2)(\mu_2\text{-}\mu_4\text{-NS}_2)]$ (**1**) as the major product.[8] Two independent molecules (**1a** and **1b**) of very similar structures were found in the crystals of **1** (see Figure 1). Both molecules show a planar Cu_4 core to which three dppm and one NS_2^{2-} coordinate in the equatorial positions. The other NS_2^{2-} (axial) is nearly perpendicular to the plane of the Cu_4 core. The four Cu ions form an irregular quadrangle; the Cu(3)−Cu(4) distance of 2.641(2) Å is shorter than the distances between Cu(1)−Cu(2) (3.074(2) Å) and Cu(1)−Cu(4) (3.335(2) Å). This difference in metal−metal distance could be due to electronic effects[9] as the Cu(3) and Cu(4) ions are bridged by μ_2-S(3) and μ_2-S(4) and a μ_4-S(4) but the Cu(1) and Cu(2) are only bridged by one μ_2-S(1) and one μ_4-S(2). Of particular interest is the S(2) atom which is almost

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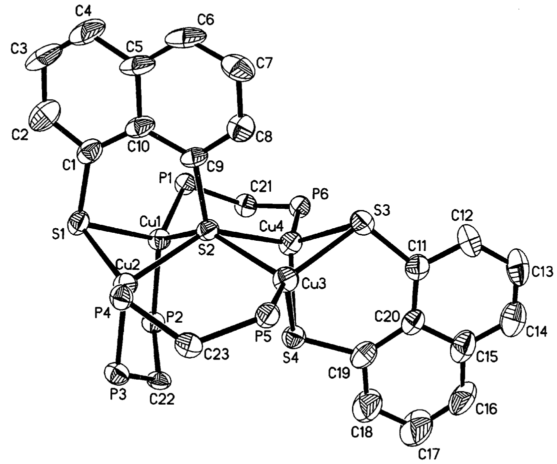

Figure 1. ORTEP plot of **1a** (thermal ellipsoid = 50%) in the crystal of **1**$\cdot$1.5CH_2Cl_2. All the phenyl rings of dppm, CH_2Cl_2, and H atoms are moved for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−S(1) 2.378(2), Cu(2)−S(1) 2.357(2), Cu(1)−S(2) 2.392(2), Cu(2)−S(2) 2.392(2), Cu(3)−S(2) 2.448(2), Cu(4)−S(2) 2.419(2), Cu(3)−S(3) 2.356(2), Cu(4)−S(3) 2.424(2), Cu(3)−S(4) 2.321(2), Cu(4)−S(4) 2.341(2), Cu(1)−P(1) 2.284(2), Cu(1)−P(2) 2.272(2), Cu(3)−P(5) 2.189(2), Cu(1)−Cu(2) 3.074(2), Cu(2)−Cu(3) 3.709(2), Cu(3)−Cu(4) 2.641(2), Cu(4)−Cu(1) 3.335(2), Cu(1)−S(1)−Cu(2) 80.95(7), Cu(1)−S(2)−Cu(2) 79.97(7), Cu(3)−S(2)−Cu(4) 65.71(6), Cu(2)−S(2)−Cu(3) 100.04(7), Cu(1)−S(2)−Cu(4) 87.77(6), Cu(3)−S(3)−Cu(4) 67.06(6), Cu(3)−S(4)−Cu(4) 68.99(6).

equidistant from the four Cu ions (Cu−S(2) = 2.392(2)−2.448(2)Å). The Cu−μ_4-S(2) distances are close to the Cu−μ_2-S distances (2.321(2)−2.424(2) Å), and similar bond distances are observed in other polynuclear Cu^I−thiolate complexes such as $[Cu_2(PPh_3)_4(\mu_2\text{-}SPh)_2]$ (Cu−S = 2.34 and 2.42 Å).[3d] The S(2) coordinating to four Cu^I ions makes **1** the first compound which features a pentacoordinate sulfur. The bridging Cu−S−Cu angles range from 67.06(6)° to 80.95(7)°. These values are close to the Cu−S−Cu angles (70−80°) found in some Cu^I complexes which contain bridging thiolates.[3−5]

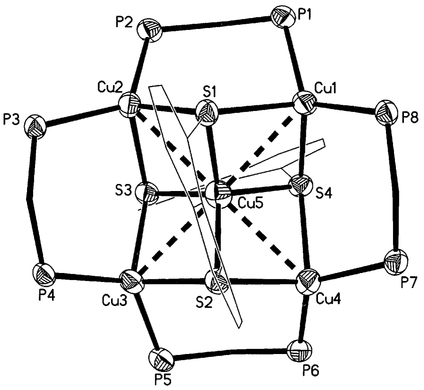

Figure 2. ORTEP plot of **2**$\cdot PF_6\cdot Et_2O\cdot$1.8$CH_2Cl_2$ (thermal ellipsoid = 50%). All the H atoms, phenyl rings, solvent molecules, and anions are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−S(4) 2.3233(1), Cu(1)−S(1) 2.5182(1), Cu(4)−S(2) 2.3103(1), Cu(4)−S(4) 2.5685(1), Cu(2)−S(1) 2.3539(1), Cu(2)−S(1) 2.3539(1), Cu(2)−S(3) 2.4702(1), Cu(3)−S(3) 2.3362(1), Cu(3)−S(2) 2.5377(1), Cu(5)−S(1) 2.2826(1), Cu(5)−S(2) 2.2721(1), Cu(5)−S(3) 2.2844(1), Cu(5)−S(4) 2.2781(1), Cu(1)−Cu(2) 3.881(1), Cu(2)−Cu(3) 3.904(1), Cu(3)−Cu(4) 3.934(1), Cu(4)−Cu(1) 3.897(1), Cu(5)−Cu(1) 2.752(1), Cu(5)−Cu(2) 2.790(1), Cu(5)−Cu(3) 2.747(1), Cu(5)−Cu(4) 2.752(1), Cu(1)−P(8) 2.24839(1), Cu(1)−S(1)−Cu(2) 105.58(5), S(3)−Cu(5)−S(2) 114.25(5), S(3)−Cu(5)−S(1) 111.36(5), S(1)−Cu(5)−S(4) 113.14(5), S(4)−Cu(5)−S(2) 114.26(5), P(1)−Cu(1)−P(8) 123.67(5), Cu(1)−Cu(5)−Cu(5) 88.92(2).

When the reaction of NS_2^{2-} and $[Cu_2(\mu_2\text{-}dppm)_2(CH_3CN)_2](PF_6)_2$ was carried out in refluxing THF for 4 h, another complex, $[Cu_5(\mu_2\text{-}dppm)_4(\mu_3\text{-}\mu_3\text{-}NS_2)_2]PF_6$ (**2**$\cdot PF_6$), was produced in moderate yield.[8,10] The most intriguing structural feature of the complex as revealed by X-ray crystallography is a square Cu_5 core which consists of four Cu ions at the corners and one Cu ion at the center of the square (Figure 2). The Cu_5 core, which is essentially planar, is connected to four equatorial dppm moieties and two axial NS_2^{2-} groups whose naphthalene rings are nearly orthogonal to each other with their planes slightly deviated from the middle lines of the square. The dppm moieties are bent from the plane of Cu_5, showing an alternate "up−down" conformation. This gives the molecule a saddlelike configuration as observed in $[Cu_4(\mu_2\text{-}dppm)_4(\mu_2\text{-}CS_3)_2]$[4b] and $[Cu_4(\mu_2\text{-}dppm)_4(\mu_4\text{-}S)]^{2+}$.[2b] The Cu−P bond lengths are similar to those found in **1**. Each sulfur atom of the two dithiolates bridges two Cu ions on each side of the square. The bridging is slightly asymmetric as the S atom is closer to one of the Cu ions than the other (e.g., Cu(1)−S(1) = 2.5182(1) Å and Cu(2)−S(1) = 2.3539(1) Å). As a result, the complex shows an approximate S_4 symmetry with the S_4 axis passing through the central Cu ion which is also the center of inversion. Notably, the molecular structure of the cation $\mathbf{2}^+$ is surprisingly similar to those of $[Cu_4(\mu_2\text{-}dppm)_4(\mu_2\text{-}CS_3)_2]$[4b] and $\{Cu_4(\mu_2\text{-}dppm)_4[\mu_2\text{-}S_2CC(CN)P(O)(OEt)_2]_2\}$;[4c] both feature a square Cu_4 capped symmetrically by two 1,1-ditholate ions. However, the Cu−Cu distances between the peripheral Cu ions in $\mathbf{2}^+$ (3.881(2)−3.934(2) Å) are much longer than the corresponding ones in $Cu_4(\mu_2\text{-}dppm)_4(\mu_2\text{-}CS_3)_2$ (3.305(6)−3.32(6) Å)[4b] and $\{Cu_4(\mu_2\text{-}dppm)_4[\mu_2\text{-}S_2CC(CN)P(O)(OEt)_2]_2\}$ (3.186−3.595 Å).[4c] Apparently, the parallel orientation of the two C−S bonds and the longer distance between the two S atoms in NS_2^{2-} allow the $Cu_4S_4P_6$ scaffold to undergo expansion to accommodate the fifth Cu ion. The central Cu(5) ion is coordinated to the four sulfur atoms in a tetrahedral geometry

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(8) Synthesis of **1**: $NaBH_4$ (0.024 g, 0.5 mmol) was added to a THF solution of naphtho[1, 8-cd]-1,2-dithiole (0.10 g, 0.5 mmol). The mixture was stirred for 30 min, and the color of the solution changed from red to colorless. The solution was transferred to a Schlenk flask containing $[Cu_2(\mu_2\text{-}dppm)_2(MeCN)_2](PF_6)_2$ (1.18 g, 1 mmol). After stirring for 1 h, the solution was filtered. The filtrate was treated with excess diethyl ether to precipitate the product as orange solids. Orange crystals were obtained from slow diffusion of Et_2O into a CH_2Cl_2/MeOH (1:1) solution of the compound. Yield: 50.0% Anal. Calcd (%) for $(C_{95}H_{78}Cu_4P_6S_4)\cdot 0.5CH_2Cl_2$: C, 62.65; H, 4.35, S, 7.01. Found (%): C, 62.24; H, 4.25; S, 6.57. ^1H NMR (500 MHz, CD_2Cl_2, δ/ppm): 9.20−6.14 (m, 72H, Ph and naphthalene H), 1.13−3.18 (m, 6H, CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, δ/ppm): −8.75 (d, 2P), −12.05 (m, 2P), −22.04 (d, 2P). Synthesis of **2**$\cdot PF_6$: The synthetic procedure for compound **2**$\cdot PF_6$ is similar to that of compound **1** except the THF solution of $[Cu_2(\mu_2\text{-}dppm)_2(MeCN)_2](PF_6)_2$ and NS_2^{2-} was refluxed for 4 h. Yellow crystals were obtained from slow diffusion of Et_2O into a CH_2Cl_2/MeOH (1:1) solution of the compound. Yield: 37.8%. Anal. Calcd (%) for $C_{120}H_{100}Cu_5F_6P_9S_4$: C, 60.54; H, 4.20; S, 5.29. Found (%): C, 60.15; H, 4.07, S, 5.32. ^1H NMR (500 MHz, CD_2Cl_2, δ/ppm): 8.08−6.26 (m, 92H, Ph and naphthalene H), 2.60−3.10 (m, 8H, CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, NMR, CD_2Cl_2, δ/ppm): −13.0 (s).

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(10) Attempts to synthesize compound **2** from refluxing a THF solution of either compound **1** or a mixture of compound **1** and $[Cu_2(dppm)_2(CH_3CN)_2](PF_6)_2$ (1:1) proved unsuccessful.

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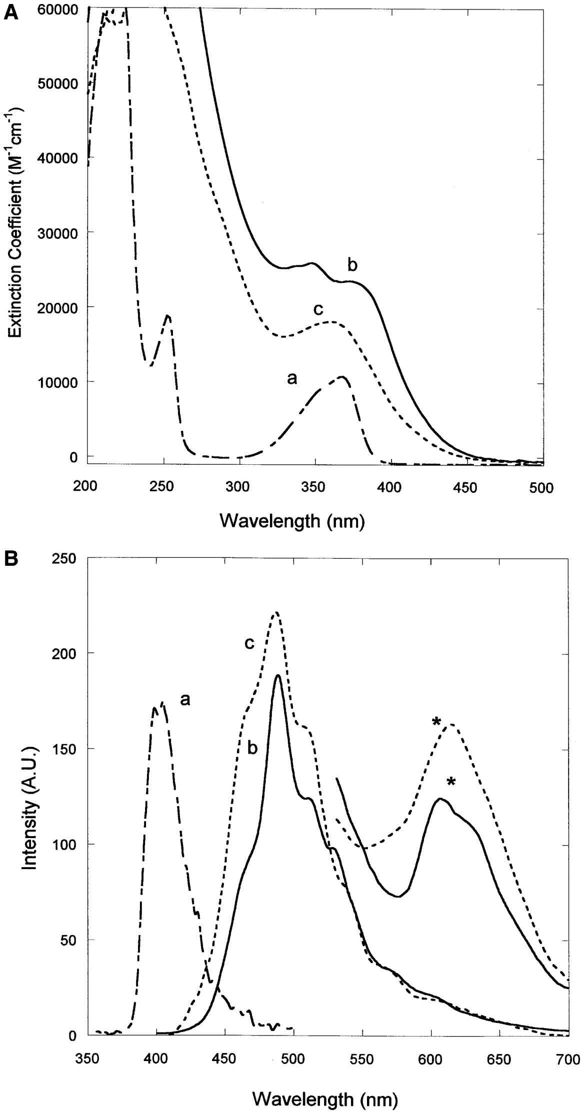

Figure 3. A. UV–vis absorption spectra of (a) NS_2 (– - –), (b) **1** (—), and (c) **2**$\cdot PF_6$ (- - -) in CH_3CN at room temperature in CH_3CN. B. Emission spectra of degassed CH_3CN solutions of (a) NS_2 (– - –), (b) **1** (—), and (c) **2**$\cdot PF_6$ (- - -): excitation wavelength = 380 nm, excitation and emission slit widths = 5 nm. Asterisk indicates enhanced emission at 620 nm at excitation wavelength = 450 nm.

(Cu(5)–S = 2.2721(1)–2.2844(1) Å and S–Cu–S = 102.14(5)–114.26(5)°), and accordingly, the S atoms are in μ_3-bridging mode. The fact that Cu(5)–S bond lengths are significantly shorter than the peripheral Cu–S bond length indicates stronger bonding interaction between the S atoms and the central copper atom. Moreover, the central Cu is 2.7472(8)–2.7897(8) Å away from the four peripheral Cu ions. It is known that $Cu^I\cdots Cu^I$ interaction is possible within such distances.[11] An interesting way to interpret the structure is to consider the Cu_4S_4 core as a metallacrown[12] which traps a Cu ion in the center via S–Cu coordination and possibly cuprophilic interactions. The few reported Cu^I_5 complexes show regular bipyramidal (e.g., $[Cu_5(\mu_2\text{-S}^t\text{Bu})_6]^-$)[3a] or open cubane (e.g., $[Cu_5(\mu_2\text{-SPh})_7]^{2-}$)[3b] metal cores. As far as we are aware, the 2-D array Cu_5 exhibited by $\mathbf{2}^+$ is unprecedented. The S_4 symmetry observed in the X-ray crystal structure could have resulted from crystal packing as the solution $^{31}P\{^1H\}$ NMR spectrum of the complex exhibits a singlet at −13.0 ppm. This indicates that the complex reverts to a higher symmetry, i.e., D_{2d}, where all the P atoms are equivalent.

The electronic absorption spectra of **1** and **2**$\cdot PF_6$ display intense bands at 375 nm ($\epsilon_{max} = 2.3 \times 10^4$ M^{-1} cm^{-1}) and 360 nm ($\epsilon_{max} = 1.8 \times 10^4$ M^{-1} cm^{-1}), respectively (Figure 3A). It is noted that, apart from an intense $\pi \rightarrow \pi^*$ transition at 252 nm ($\epsilon_{max} = 1.9 \times 10^4$ M^{-1} cm^{-1}),[13] the spectrum of NS_2 displays an absorption band at 367 nm ($\epsilon_{max} = 1.1 \times 10^4$ M^{-1} cm^{-1}) which is attributable to the n(S) $\rightarrow \pi^*$ transition. In view of the similar energy and intensity, the absorptions at 375 and 360 nm are assigned to intraligand n(S) $\rightarrow \pi^*$ transitions. While NS_2 does not absorb between 270 and 310 nm and beyond 400 nm, the two copper complexes show moderate absorption in 400–500 nm and strong absorption in 200–400 nm. Previous spectroscopic studies[2c] of $[Cu_3(\mu_2\text{-dppm})_3(\mu_3\text{-SR})(\mu_3\text{-X})]^+$ (R = alkyl or aryl, X = SR or Cl) demonstrated that the ligand(RS^-)–metal(Cu) charge-transfer (LMCT) absorption extends from 290 to 400 nm. Possibly, the 400–500 nm absorption of **1** and **2**$\cdot PF_6$ is part of an LMCT (S → Cu) transition which overlaps with the intraligand absorption.

Photoexcitation of degassed CH_3CN solution of NS_2 and of the complexes **1** and **2**$\cdot PF_6$ at 380 nm gives emissions maximized at 410 nm, and 486 and 489 nm, respectively (Figure 3B). The 410 nm emission of NS_2 is attributable to $^1(n\pi^*)$ fluorescence.[14] Poorly resolved vibronic structures with spacing of ~1100 cm^{-1} are seen in the 486 and 488 nm emissions of the complexes. The emissions are tentatively assigned to the spin forbidden $^3(n\pi^*)$ phosphorescence on the basis of the large Stokes shift between the emission and the absorption. Close inspection of the emission spectra of the complexes reveals a weak emission band around 620 nm whose intensities increase as the excitation wavelength is changed from 380 to 450 nm. Notably, emissions of similar energy, which are assigned to the ^{3}LMCT excited state,[2] have been widely observed for polynuclear Cu^I–thiolates such as $[Cu_3(\mu_2\text{-dppm})_3(\mu_3\text{-SR})(\mu_3\text{-X})]^+$ (λ_{em} = 610 nm)[2c] and $[Cu(SC_6H_4\text{-2-}CH_2NMe_2)]_3$ (λ_{em} = 610 nm).[2f] Accordingly, the 620 nm luminescence of the present complexes could arise from an ^{3}LMCT (S → Cu) excited state.

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Supporting Information Available: Experimental procedures and the X-ray crystallographic data in CIF format for **1**$\cdot 1.5CH_2Cl_2$ and **2**$\cdot PF_6\cdot Et_2O\cdot 1.8CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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