Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Material

Synthesis and Characterization of an Octanuclear Copper(I) Methanediide Cluster

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The Supplementary Material contains:

1. Experimental Section
2. X-ray crystallographic data for compound **3**
3. Selected bond distances and angles for compound **3**
4. Absorption, emission and excitation spectra of compound **3**

Experimental Section

General procedures. All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from Na (Et_2O and THF). $[K\{CH(^iPr_2P\text{-}S)(C_9H_6N\text{-}2)\}]_n$ was prepared according to the literature procedures.[1] CuCl was purchased from Aldrich Chemical Co. and used without further purification. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on Bruker 400 spectrometer. The NMR spectra were recorded in C_6D_6, and the chemical shift are relative to $SiMe_4$ for ^1H and $^{13}C\{^1H\}$ and 85% H_3PO_4 for $^{31}P\{^1H\}$, respectively.

Synthesis of 3

A solution of **1** (1.04 g, 3.16 mmol) in THF (30ml) was added to a solution of CuCl (0.31 g, 3.13 mmol) in THF (10ml) at 0 °C. The reaction mixture was stirred at room temperature for 12 hr and red mixture was formed. All the volatiles in the reaction mixture were removed under reduced pressure and the residue was extracted with Et_2O (20 ml). After filtration, THF (10 ml) was added to the filtrate and the filtrate was concentrated, compound **3** was isolated as red crystals. Yield: 0.36 g (55.2 %). Mp: 294.8 °C. Anal. Found: C, 46.33 ; H, 5.32 ; N, 3.36 Calcd. For $C_{64}H_{80}Cu_8N_4P_4S_4$: C, 46.14 ; H, 4.85 ; N, 3.36. ^1H NMR (C_6D_6, 25 °C): δ =

1.05-1.15 (m, 12H, CH*Me*$_2$), 1.81-2.16 (m, 2H, C*H*Me$_2$), 6.58 (d, 1H, J_{H-H} = 8 Hz, Qu), 6.96 (t, 1H, Qu), 7.28 (d, 1H, J_{H-H} = 8 Hz, Qu), 7.35 (t, 1H, J_{H-H} = 8 Hz, Qu), 7.48 (t, 1H, J_{H-H} = 8 Hz, Qu), 8.87 (d, 1H, J_{H-H} = 12 Hz, Qu) $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 18.9 (CH*Me*$_2$), 30.4 (*C*HMe$_2$), 66.1 (CuCCu), 121.0, 122.3, 123.6, 126.8, 129.2, 133.6, 136.2, 147.7, 171.9 (Qu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 61.7.

X-ray crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **3** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50kV and 90mA. The structures were solved by direct phase determination using the computer program SHELXTL-PC on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms.[2] Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations.

Table 1. Crystallographic Data for Compound **3**

	3
Formula	$C_{64}H_{80}Cu_8N_4P_4S_4$
Fw	1665.76
Color	Red
Cryst. Syst.	Monoclinic
Space Group	$P2_1/c$
a (Å)	12.961(1)
b (Å)	12.923(1)
c (Å)	46.063(4)
α (deg)	90
β (deg)	90.277(2)
γ (deg)	90
V (Å^3)	7715.1(1)
Z	4
d_{calcd} (g cm^{-3})	1.434
μ (mm^{-1})	2.389
F(000)	3392
Cryst size (mm)	0.50 x 0.40 x 0.30
2θ range (deg)	0.88 to 25.25
Index range	$-15 \leq h \leq 15$, $-7 \leq k \leq 15$, $-55 \leq l \leq 55$
No. of rflns collected	60540
No. of indep rflns	13971
R1, wR2 ($I > 2(\sigma)I$)	0.0401, 0.0962
R1, wR2 (all data)	0.0643, 0.1085
Goodness of fit, F^2	1.053
No. of data/restraints /params	3135 / 0 / 181
Largest diff peaks ,eÅ^{-3}	0.724 to -0.521

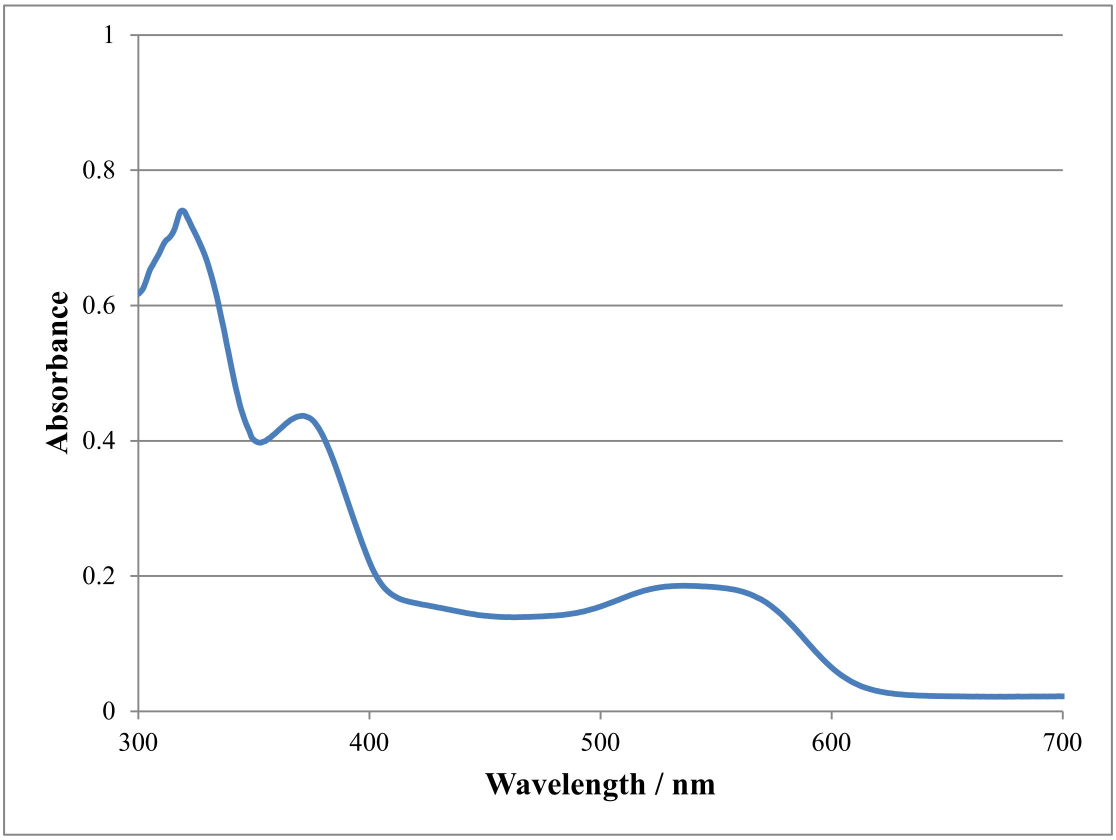
Table 1 Selected Bond Distances (Å) and Angles (deg) for Compound 3

Cu(1)-N(1)	1.974(6)	Cu(4)-Cu(6)	2.660(2)
Cu(1)-S(3)	2.302(2)	Cu(5)-C(10)	1.983(8)
Cu(1)-S(4)	2.338(2)	Cu(5)-C(42)	1.996(8)
Cu(1)-Cu(5)	2.632(1)	Cu(5)-Cu(7)	2.548(1)
Cu(1)-Cu(2)	2.667(1)	Cu(5)-Cu(8)	2.551(1)
Cu(1)-Cu(8)	2.673(2)	Cu(6)-C(26)	1.966(8)
Cu(2)-N(2)	1.966(6)	Cu(6)-C(58)	1.973(8)
Cu(2)-S(4)	2.306(2)	Cu(6)-Cu(8)	2.541(1)
Cu(2)-S(3)	2.348(2)	Cu(6)-Cu(7)	2.543(1)
Cu(2)-Cu(6)	2.637(2)	Cu(7)-C(26)	1.982(7)
Cu(2)-Cu(7)	2.667(2)	Cu(7)-C(42)	1.991(8)
Cu(3)-N(3)	1.964(7)	Cu(8)-C(58)	1.961(7)
Cu(3)-S(2)	2.310(3)	Cu(8)-C(10)	1.997(8)
Cu(3)-S(1)	2.322(3)	P(1)-C(10)	1.753(8)
Cu(3)-Cu(7)	2.638(2)	P(1)-S(1)	2.026(3)
Cu(3)-Cu(5)	2.648(2)	P(2)-C(26)	1.751(8)
Cu(3)-Cu(4)	2.703(2)	P(2)-S(2)	2.033(3)
Cu(4)-N(4)	1.949(7)	P(3)-C(42)	1.739(8)
Cu(4)-S(1)	2.315(3)	P(3)-S(3)	2.034(3)
Cu(4)-S(2)	2.329(2)	P(4)-C(58)	1.775(8)
Cu(4)-Cu(8)	2.632(1)	P(4)-S(4)	2.033(3)
N(1)-Cu(1)-S(3)	131.3(2)	Cu(7)-Cu(6)-Cu(2)	61.9(4)
N(1)-Cu(1)-S(4)	124.6(2)	C(26)-Cu(6)-Cu(4)	107.0(2)
S(3)-Cu(1)-S(4)	93.6(8)	C(58)-Cu(6)-Cu(4)	76.6(2)
N(1)-Cu(1)-Cu(5)	85.1(2)	Cu(8)-Cu(6)-Cu(4)	60.8(4)
S(3)-Cu(1)-Cu(5)	90.6(7)	Cu(7)-Cu(6)-Cu(4)	92.2(4)
S(3)-Cu(1)-Cu(2)	55.8(6)	C(26)-Cu(7)-Cu(6)	49.6(2)
S(4)-Cu(1)-Cu(2)	54.4(6)	C(42)-Cu(7)-Cu(5)	50.4(2)
Cu(5)-Cu(1)-Cu(2)	90.4(4)	Cu(6)-Cu(7)-Cu(5)	90.4(4)
N(1)-Cu(1)-Cu(8)	84.5(2)	C(26)-Cu(7)-Cu(3)	104.5(2)
S(3)-Cu(1)-Cu(8)	132.0(7)	C(42)-Cu(7)-Cu(3)	77.8(2)
S(4)-Cu(1)-Cu(8)	85.6(7)	Cu(6)-Cu(7)-Cu(3)	91.3(4)
Cu(5)-Cu(1)-Cu(8)	57.5(4)	Cu(5)-Cu(7)-Cu(3)	61.4(4)
Cu(2)-Cu(1)-Cu(8)	87.0(4)	C(26)-Cu(7)-Cu(2)	77.3(2)
N(2)-Cu(2)-S(3)	125.8(2)	C(42)-Cu(7)-Cu(2)	106.7(2)

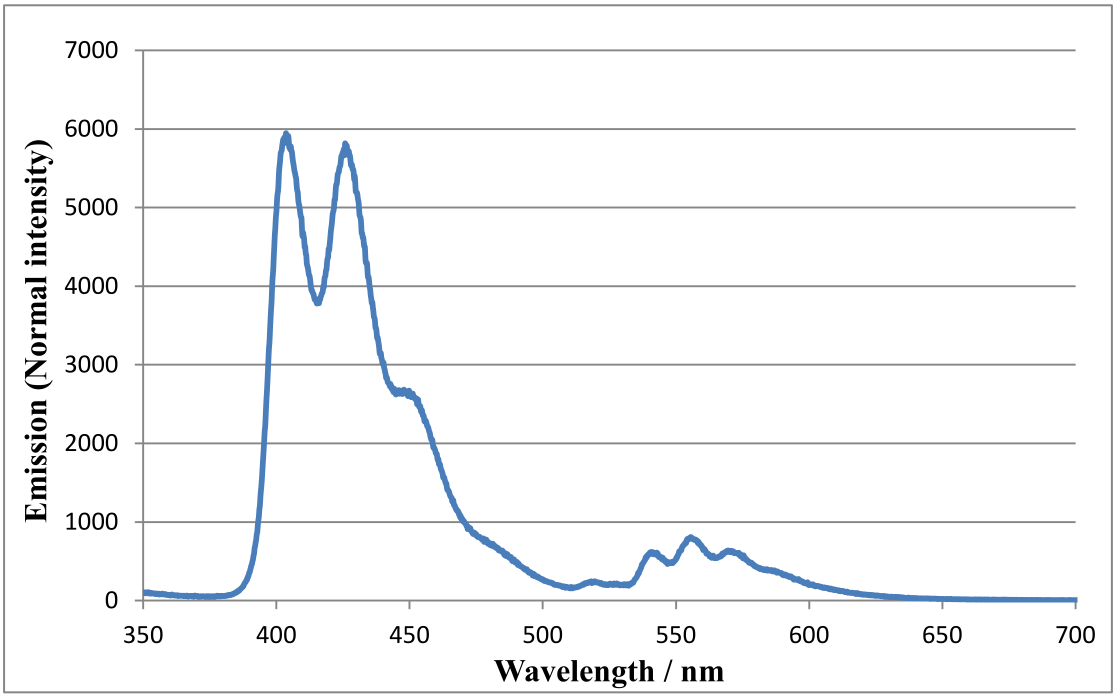
N(2)-Cu(2)-S(4)	130.8(2)	Cu(6)-Cu(7)-Cu(2)	60.8(4)
S(4)-Cu(2)-S(3)	93.2(8)	Cu(5)-Cu(7)-Cu(2)	92.2(4)
N(2)-Cu(2)-Cu(6)	84.7(2)	C(58)-Cu(8)-Cu(6)	50.0(2)
S(3)-Cu(2)-Cu(6)	131.7(7)	C(10)-Cu(8)-Cu(5)	49.9(2)
S(4)-Cu(2)-Cu(6)	90.0(7)	Cu(6)-Cu(8)-Cu(5)	90.4(4)
S(3)-Cu(2)-Cu(1)	54.2(6)	C(58)-Cu(8)-Cu(4)	77.4(2)
S(4)-Cu(2)-Cu(1)	55.5(6)	C(10)-Cu(8)-Cu(4)	104.0(2)
Cu(6)-Cu(2)-Cu(1)	90.3(5)	Cu(6)-Cu(8)-Cu(4)	61.9(4)
N(2)-Cu(2)-Cu(7)	84.8(2)	Cu(5)-Cu(8)-Cu(4)	90.9(4)
S(3)-Cu(2)-Cu(7)	86.2(7)	C(58)-Cu(8)-Cu(1)	107.7(2)
S(4)-Cu(2)-Cu(7)	131.4(7)	C(10)-Cu(8)-Cu(1)	77.1(2)
Cu(1)-Cu(2)-Cu(7)	87.0(4)	Cu(6)-Cu(8)-Cu(1)	92.2(4)
Cu(6)-Cu(2)-Cu(7)	57.3(4)	Cu(5)-Cu(8)-Cu(1)	60.4(4)
N(3)-Cu(3)-S(1)	128.0(2)	C(10)-P(1)-S(1)	111.6(3)
N(3)-Cu(3)-S(2)	129.3(2)	C(26)-P(2)-S(2)	110.6(3)
S(2)-Cu(3)-S(1)	92.7(9)	C(42)-P(3)-S(3)	111.9(3)
N(3)-Cu(3)-Cu(7)	84.9(2)	C(58)-P(4)-S(4)	111.0(3)
S(1)-Cu(3)-Cu(7)	131.2(8)	P(1)-S(1)-Cu(4)	106.6(1)
S(2)-Cu(3)-Cu(7)	88.8(7)	P(1)-S(1)-Cu(3)	112.4(1)
N(3)-Cu(3)-Cu(5)	85.8(2)	Cu(4)-S(1)-Cu(3)	71.3(8)
S(1)-Cu(3)-Cu(5)	86.6(7)	P(2)-S(2)-Cu(3)	107.7(1)
S(2)-Cu(3)-Cu(5)	131.0(8)	P(2)-S(2)-Cu(4)	112.7(1)
Cu(7)-Cu(3)-Cu(5)	57.6(4)	Cu(3)-S(2)-Cu(4)	71.3(7)
S(1)-Cu(3)-Cu(4)	54.2(7)	P(3)-S(3)-Cu(1)	106.8(1)
S(2)-Cu(3)-Cu(4)	54.7(7)	P(3)-S(3)-Cu(2)	111.8(1)
Cu(5)-Cu(3)-Cu(4)	87.4(5)	Cu(1)-S(3)-Cu(2)	70.0(7)
N(4)-Cu(4)-S(1)	130.2(2)	P(4)-S(4)-Cu(2)	107.0(1)
N(4)-Cu(4)-S(2)	127.8(2)	P(4)-S(4)-Cu(1)	112.8(1)
S(1)-Cu(4)-S(2)	92.3(9)	Cu(2)-S(4)-Cu(1)	70.09(7)
N(4)-Cu(4)-Cu(8)	84.4(2)	C(1)-N(1)-Cu(1)	116.9(5)
S(1)-Cu(4)-Cu(8)	89.8(7)	C(17)-N(2)-Cu(2)	117.5(5)
S(2)-Cu(4)-Cu(8)	130.5(7)	C(33)-N(3)-Cu(3)	117.0(5)
N(4)-Cu(4)-Cu(6)	85.1(2)	C(49)-N(4)-Cu(4)	118.4(5)
S(1)-Cu(4)-Cu(6)	131.3(8)	C(1)-C(10)-P(1)	121.9(6)
S(2)-Cu(4)-Cu(6)	86.0(7)	C(1)-C(10)-Cu(5)	115.5(6)
Cu(8)-Cu(4)-Cu(6)	57.4(4)	P(1)-C(10)-Cu(5)	110.2(4)
S(1)-Cu(4)-Cu(3)	54.5(7)	C(1)-C(10)-Cu(8)	112.5(6)
S(2)-Cu(4)-Cu(3)	54.0(7)	P(1)-C(10)-Cu(8)	109.1(4)

Cu(6)-Cu(4)-Cu(3)	87.4(5)	Cu(5)-C(10)-Cu(8)	79.7(3)
Cu(8)-Cu(4)-Cu(3)	89.3(5)	C(17)-C(26)-P(2)	119.7(6)
C(42)-Cu(5)-Cu(7)	50.2(2)	C(17)-C(26)-Cu(6)	114.7(5)
C(10)-Cu(5)-Cu(8)	50.4(2)	P(2)-C(26)-Cu(6)	110.9(4)
Cu(7)-Cu(5)-Cu(8)	89.4(4)	C(17)-C(26)-Cu(7)	115.3(6)
C(10)-Cu(5)-Cu(1)	78.4(2)	P(2)-C(26)-Cu(7)	109.4(4)
C(42)-Cu(5)-Cu(1)	103.1(2)	Cu(6)-C(26)-Cu(7)	80.2(3)
Cu(7)-Cu(5)-Cu(1)	90.3(4)	C(33)-C(42)-P(3)	120.6(6)
Cu(8)-Cu(5)-Cu(1)	62.1(4)	C(33)-C(42)-Cu(7)	115.0(5)
C(10)-Cu(5)-Cu(3)	107.0(2)	P(3)-C(42)-Cu(7)	110.1(4)
C(42)-Cu(5)-Cu(3)	77.5(2)	C(33)-C(42)-Cu(5)	114.0(6)
Cu(7)-Cu(5)-Cu(3)	61.0(4)	P(3)-C(42)-Cu(5)	110.5(4)
Cu(8)-Cu(5)-Cu(3)	92.3(4)	Cu(7)-C(42)-Cu(5)	79.4(3)
C(58)-Cu(6)-Cu(8)	49.6(2)	C(49)-C(58)-P(4)	118.1(6)
C(26)-Cu(6)-Cu(7)	50.2(2)	C(49)-C(58)-Cu(8)	117.2(6)
Cu(8)-Cu(6)-Cu(7)	89.8(4)	P(4)-C(58)-Cu(8)	109.6(4)
C(26)-Cu(6)-Cu(2)	78.2(2)	C(49)-C(58)-Cu(6)	115.7(6)
C(58)-Cu(6)-Cu(2)	104.0(2)	P(4)-C(58)-Cu(6)	109.8(4)
Cu(8)-Cu(6)-Cu(2)	90.4(4)	Cu(8)-C(58)-Cu(6)	80.4(3)

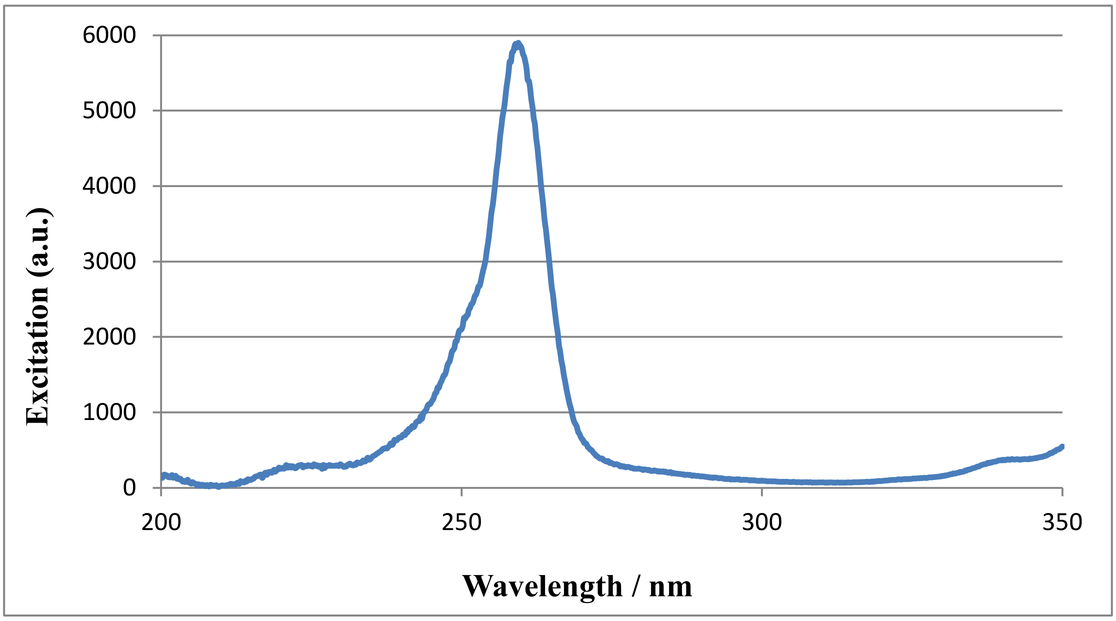
Absorption spectrum of compound 3



Emission spectrum of compound 3



Excitation spectrum of compound 3



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