Electronic Supplementary Material

Contents

1. Electronic Structure

The electronic spectra of Cu^{2+} acetate complexes of ligands **1-6** (**Table S1**) have a charge transfer band with high extinction coefficient in the range of λ_{max} = 274-306 nm (ε = 5,130-6,490 M^{-1} cm^{-1}). The expected low intensity d-d transition occurs in a range of λ_{max} = 668-728 nm (ε = 120-190 M^{-1} cm^{-1}).

Table S1. Electronic spectra of Cu^{2+} complexes

Complex	**Absorption wavelength in nm (extinction coefficient M^{-1} cm^{-1})**	
	CT band	d-d band
[Cu**1**(OAc)]$^+$	274 (6,930)	668 (170)
[Cu**2**(OAc)]$^+$	284 (7,500)	686 (180)
[Cu**3**(OAc)]$^+$	275 (5,130)	687 (120)
[Cu**4**(OAc)]$^+$	298 (5,900)	692 (190)
[Cu**5**(OAc)]$^+$	306 (6,930)	708 (150)
[Cu**6**(OAc)]$^+$	306 (6,490)	728 (140)

2. Crystallography

Table S2. Crytal Data and Structural Refinement Details

formula	$CuC_{14}H_{29}N_4F_6O_2P$	$Cu_2C_{30}H_{50}N_4O_7$	$CuC_{29.50}H_{44}N_4O_{2.50}PF_6$	$ZnC_{14}H_{31}N_4O_3PF_6$	$ZnC_{16}H_{35}N_4O_3PF_6$	$CuC_{12}H_{29}N_4Cl_5$	$CuC_{13}H_{30}N_4O_5$
formual wt.	493.92	642.29	703.20	513.77	541.82	470.19	385.95
space group	P21/c	P-1	P-1	$I4_1/a$	R3c	Pbcm	$Pna2_1$
a(Å)	7.5846(7)	9.8111(12)	9.4251(13)	15.6365(7)	26.0448(15)	7.5065(7)	16.7675(5)
b(Å)	16.8061(13)	13.5031(16)	12.7961(18)	15.6365(7)	26.0448(15)	13.3171(14)	8.2529(9)
c(Å)	15.5964(14)	13.8120(18)	14.563(2)	35.497(2)	17.2741(13)	19.872(3)	11.6715(12)
α(deg)	90	64.046(9)	70.445(11)	90	90	90	90
ß(deg)	94.815(7)	81.789(10)	74.872(11)	90	90	90	90
γ(deg)	90	69.567(9)	89.690(11)	90	120	90	90
V(Å^3)	1981.0(3)	1541.6(3)	1591.2(4)	8679.0(8)	10147.7(11)	1986.5(4)	1615.1(2)
Z	4	2	2	16	18	4	4
ρ_{calc}(g/cm^3)	1.656	1.384	1.468	1.573	1.596	1.572	1.587
temp(K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
wavelength(Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
abs. coeff.(mm^{-1})	1.256	0.760	0.808	1.279	1.235	1.773	1.384
R1(F_o^2) =	0.0399	0.0897	0.0580	0.0390	0.0371	0.0451	0.0417
wR2(F_o^2) =	0.0860	0.2757	0.1812	0.0903	0.0722	0.1237	0.1177

[a]$[I > 2\sigma(I)$ [b]$wR1 = \Sigma||F_o| - |F_c||/|F_o|$ [c]$wR2 = \{\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$ $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$

Table S3. Selected bond lengths [Å] and angles [º]:

[Cu(**2**)(OAc)][PF_6]

Cu(1)-N(3)	2.014(2)	Cu(1)-N(4)	2.0830(18)
Cu(1)-N(1)	2.164(2)	Cu(1)-O(1)	1.9565(17)
Cu(1)-N(2)	2.0722(18)	Cu(1)-O(2)	2.576
N(4)-Cu(1)-N(2)	164.04(8)	N(2)-Cu(1)-N(1)	81.72(7)
N(4)-Cu(1)-N(1)	85.54(7)	O(1)-Cu(1)-N(1)	111.36(8)
N(4)-Cu(1)-N(3)	83.15(8)	O(1)-Cu(1)-N(2)	95.34(7)
N(3)-Cu(1)-N(2)	86.18(8)	O(1)-Cu(1)-N(3)	163.63(8)
N(3)-Cu(1)-N(1)	85.00(8)	O(1)-Cu(1)-N(4)	98.25(7)

[Cu(**5**)(OAc)][OAc]

N(1)-Cu(1)	2.187(2)	N(4)-Cu(1)	2.040(2)
N(2)-Cu(1)	2.190(8)	Cu(1)-O(1)	1.9592(18)
N(3)-Cu(1)	2.107(2)	Cu(1)-O(2)	2.794
O(1)-Cu(1)-N(4)	160.45(9)	N(3)-Cu(1)-N(1)	176.11(8)
O(1)-Cu(1)-N(3)	88.47(8)	O(1)-Cu(1)-N(2)	112.85(9)
N(4)-Cu(1)-N(3)	85.49(9)	N(4)-Cu(1)-N(2)	86.05(9)
O(1)-Cu(1)-N(1)	94.36(8)	N(3)-Cu(1)-N(2)	92.91(9)
N(4)-Cu(1)-N(1)	92.67(9)	N(1)-Cu(1)-N(2)	83.53(9)

[Cu(**5**)(OAc)][PF_6]

N(1)-Cu(1)	2.147(2)	N(4)-Cu(1)	2.056(2)
N(2)-Cu(1)	2.175(2)	Cu(1)-O(1)	1.9469(18)
N(3)-Cu(1)	2.104(2)	Cu(1)-O(2)	2.887
O(1)-Cu(1)-N(4)	165.23(8)	N(3)-Cu(1)-N(1)	176.74(8)
O(1)-Cu(1)-N(3)	88.09(8)	O(1)-Cu(1)-N(2)	107.51(8)
N(4)-Cu(1)-N(3)	84.85(9)	N(4)-Cu(1)-N(2)	85.93(8)
O(1)-Cu(1)-N(1)	94.66(8)	N(3)-Cu(1)-N(2)	93.86(8)
N(4)-Cu(1)-N(1)	92.86(8)	N(1)-Cu(1)-N(2)	83.64(8)

Zn(**2**)(OAc)(H_2O)$^+$

N(1)-Zn(1)	2.160(3)	N(4)-Zn(1)	2.183(3)
N(2)-Zn(1)	2.195(2)	O(1)-Zn(1)	2.0524(19)
N(3)-Zn(1)	2.146(3)	O(3)-Zn(1)	2.056(2)
O(1)-Zn(1)-O(3)	90.83(8)	O(2)-H(15B)	1.79(2)
O(1)-Zn(1)-N(3)	90.31(9)	N(3)-Zn(1)-N(4)	83.81(11)
O(3)-Zn(1)-N(3)	175.89(11)	N(1)-Zn(1)-N(4)	79.40(10)
O(1)-Zn(1)-N(1)	171.61(9)	O(1)-Zn(1)-N(2)	98.44(9)
O(3)-Zn(1)-N(1)	97.24(9)	O(3)-Zn(1)-N(2)	95.98(10)
N(3)-Zn(1)-N(1)	81.80(10)	N(3)-Zn(1)-N(2)	79.95(11)
O(1)-Zn(1)-N(4)	96.99(9)	N(1)-Zn(1)-N(2)	83.07(10)
O(3)-Zn(1)-N(4)	99.96(9)	N(4)-Zn(1)-N(2)	157.59(10)

Zn(**1**)(OAc)(H_2O)$^+$

Zn(1)-N(1)	2.159(3)	Zn(1)-N(4)	2.197(3)
Zn(1)-N(2)	2.188(3)	Zn(1)-O(1)	2.062(2)
Zn(1)-N(3)	2.155(3)	Zn(1)-O(3)	2.135(3)
N(1)-Zn(1)-N(2)	83.49(11)	O(1)-Zn(1)-O(3)	88.70(10)
N(1)-Zn(1)-N(3)	83.44(11)	O(1)-Zn(1)-N(1)	171.70(11)
N(1)-Zn(1)-N(4)	89.89(11)	O(2)-H(17A)	1.75
N(2)-Zn(1)-N(3)	90.68(12)	O(1)-Zn(1)-N(2)	90.05(10)
N(2)-Zn(1)-N(4)	171.89(12)	O(1)-Zn(1)-N(3)	91.46(11)
N(3)-Zn(1)-N(4)	83.90(11)	O(1)-Zn(1)-N(4)	96.09(10)

O(3)-Zn(1)-N(1)	97.42(11)	O(3)-Zn(1)-N(3)	170.43(10)
O(3)-Zn(1)-N(2)	98.90(11)	O(3)-Zn(1)-N(4)	86.56(10)

Cu(**2**)(CO_3)

N(1)-Cu(1)	2.035(3)	N(3)-Cu(1)-N(2)	79.73(12)
N(2)-Cu(1)	2.3383(19)	N(1)-Cu(1)-N(2)	81.94(11)
N(3)-Cu(1)	2.035(3)	O(2)-Cu(1)-N(4)	101.88(11)
N(4)-Cu(1)	2.363(2)	O(1)-Cu(1)-N(4)	99.53(10)
O(2)-Cu(1)-O(1)	66.94(6)	N(3)-Cu(1)-N(4)	81.96(11)
O(2)-Cu(1)-N(3)	104.08(11)	N(1)-Cu(1)-N(4)	79.67(11)
O(1)-Cu(1)-N(3)	171.02(11)	N(2)-Cu(1)-N(4)	154.88(7)
O(2)-Cu(1)-N(1)	170.73(11)	Cu(1)-O(2)	1.994(3)
O(1)-Cu(1)-N(1)	103.81(11)	Cu(1)-O(1)	1.985(3)
N(3)-Cu(1)-N(1)	85.17(7)	O(3)-O(4)	2.890(5)
O(2)-Cu(1)-N(2)	99.03(10)	O(3)-O(5)	2.908(5)
O(1)-Cu(1)-N(2)	101.37(10)		