"3 + 1 = 6 + 2" in Cu(II) Coordination Chemistry of 1*H*-Pyrazole aza cryptands

Javier Pitarch-Jarque, Raquel Belda, Alberto Lopera, Francisco Lloret, Jesús Ferrando-Soria, Pilar Navarro and Enrique García-España.*

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Figure S0. a) ¹H NMR (400 MHz, CD₃OD) spectrum of L, b) COSY spectrum of L and c) HSQC spectrum of L.

Compound	1	2	3	4
Empirical formula	$C_{27}H_{50}Cl_2$	$C_{96}H_{180}Cu_{6}$	$C_{54}H_{94}Cu_{6}$	$C_{62}H_{128.7}Cl_6$
	$Cu_2N_{34}O_{10}$	$N_{28}O_{42}S_6$	$N_{34}O_{20}$	$Cu_6N_{34}O_{16.35.}$
Formula weight	928.79	2972.34	1920.87	2149.84
Temperature	293.0(2) K	293.0(2)	293.0(2) K	120.0(2) K
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	P 21	P -1	P cab	P 21/n
Unit cell dimensions				
a(Å)	12.3240 (4)	12.6670(2)	12.230(2)	17.2950(7)
b(Å)	10.0650 (3)	13.5270(3)	20.9780(3)	12.2060(4)
c(Å)	15.2650 (5)	21.6730(5)	29.5070(4)	23.124(1)
α(°)	90	79.750(1)	90	90
β(°)	92.552(2)	76.055(1)	90	95.390(2)
γ(°)	90	62.096(1)	90	90
Volume Å ³	1891.61(10)	3175.90(11)	7570.34(19)	4860.0(3)
Z	2	1	8	2
Density calc (g/cm ³)	1.631	1.554	1.685	1.602
Crystal size (mm)	$0.3 \times 0.2 \times 0.15$	$0.4 \times 0.3 \times 0.2$	$0.2 \times 0.15 \times 0.15$	$0.3 \times 0.2 \times 0.2$
Wavelength	0.71073	0.71073	0.71073	0.71073
F(000)	964	1558	3960	2274.2
μ (mm ⁻¹)	1.338	1.178	1.748	1.528
Absorption correction	Cylinder	Cylinder	Cylinder	Cylinder
Θrange	1.00° to 27.48°	1.70° to 25°	2.40° to 25°	1.4° to 27.5°
refins collected	8541	21630	29520	19352
indep reflns	6643	11150	8477	10887
R(int)	0.032	0.036	0.0501	0.0329
data/restr/param	6643/56/549	11150/26/842	8477/80/570	10887/94/626
Final R indices	R1 = 0.0479;	R1 = 0.0501;	R1 = 0.0428;	R1 = 0.0677;
[I >2 sigma(I)]	$wR^2 = 0.1043;$	$wR^2 = 0.1203;$	$wR^2 = 0.1101;$	$wR^2 = 0.1967;$
R indices all data	R1 = 0.0731;	R1 = 0.0649;	<i>R</i> 1=0.0770;	R1 = 0.1061;
	$wR^2 = 0.1193;$	$wR^2 = 0.1258;$	$wR^2 = 0.1255;$	$WR^2 = 0.2239;$
$GOF(F^2)$	1.050	1.084	1.028	1.014

 Table S1. Crystallographic data for complexes 1-4.

Figure S1. Ellipsoid drawing of binuclear copper(II) complex 1 (the thermal ellipsoids are set at 50% probability).

Figure S2. a, b) Ball and stick views of complex 3. C) Space-fill representation of complex 3.

Figure S3. a, b) Ball and stick views of complex 4. c) Space-fill representation of complex 4.d) View of the polymeric chain along the *a* axis (Hydrogen bonds in red).

Table S2. Stability Constants for the Formation of Cu(II) Complexes of Receptor L Determined in 0.15 mol dm⁻³ NaCl at 298.1 K.

Reaction ^a	
$Cu+L+2H \leftrightarrows CuH_2L$	$35.40(8)^{b}$
$Cu+L+H \leftrightarrows CuHL$	28.83(7)
$Cu+L \leftrightarrows CuL$	21.76(6)
$Cu+L+H_2O \leftrightarrows CuH_1L+H$	13.05(5)
$2Cu + L + H \leftrightarrows Cu_2HL$	39.04(6)
$2Cu + L \leftrightarrows Cu_2L$	36.72(4)
$2Cu + L \leftrightarrows Cu_2H_{-1}L + H$	31.34(5)
$2Cu + L \leftrightarrows Cu_2H_{-2}L + 2H$	24.15(5)
$6Cu + 2L \leftrightarrows Cu_6(H_3L)_2 + 6H$	54.85(8)
$CuHL + H \leftrightarrows CuH_2L$	6.6
CuL + H ≒ CuHL	7.1
CuL与 CuH ₋₁ L+ H	-8.7
$CuL + Cu \leftrightarrows Cu_2L$	15.0
$Cu_2L + H \leftrightarrows Cu_2HL$	2.3
$Cu_2L \leftrightarrows Cu_2H_{-1}L + H$	-5.4
$O = II I \leftarrow O = II I + II$	-72

^a Charges omitted. ^b Values in parentheses are standard deviations in the last significant figure.

Figure S4. a) UV-Vis spectra of aqueous solutions containing Cu(II):L in 3:1 molar ratio recorded as a function of pH. b) Plot of the distribution diagram of the system Cu(II):L in 3:1 molar ratio (charges omitted) with the variation of the absorption at 569 nm.

Figure S5a. HR-ESI-Ms spectrum of 3:1 Cu(II):L aqueous solutions at pH 7 in NaTsO recorded in water/methanol (50/50 vol/vol), pH = 7. [L] = 1×10^{-3} M.

Figure S5b. HR-ES-Ms spectrum of 3:1 Cu(II):L aqueous solutions at pH 7 in NaTsO recorded in water/methanol (50/50 vol/vol), pH = 7 in the m/z = 750 - 1400 range.

Figure S5c. Simulated (top) and experimental (bottom) HR-ESI-MS peaks for $[NaCu_6(H_3L)_2(TsO)_4]^{3+}$. HR-ES-Ms spectra recorded in water/methanol (50/50 vol/vol), pH = 7.

Figure S5d. Simulated (top) and experimental (bottom) HR-ESI-MS peaks for $[Na_2Cu_6(H_3L)_2(TsO)_5]^{3+}$. HR-ESI-Ms spectra recorded in water/methanol (50/50 vol/vol), pH = 7.

Figure S5e. Simulated (top) and experimental (bottom) HR-ESI-MS peaks for $[Na_3Cu_6(H_3L)_2(TsO)_6]^{3+}$. HR-ESI-Ms spectra recorded in water/methanol (50/50 vol/vol), pH = 7.

Magnetic Properties of binuclear copper(II) complex 1.

The magnetic properties of **1** are shown in Figure in the form of $\chi_M T$ versus *T*, χ_M being the magnetic susceptibility per two copper(II) ions. The value of $\chi_M T$ at room temperature is 0.45 cm³.mol⁻¹ K, this value is significantly lower than the expected for two uncoupled Cu(II) ions. When the sample is cooling $\chi_M T$ continuously decreases, vanishing at around 70 K. This magnetic behaviour is characteristic of an important antiferromagnetic interaction between the Cu(II) ions with singlet spin ground state.

Given that the interaction between dinuclear subunits is expected to be very weak, it is reasonable to assume that the magnetic properties are determined by the coupling within dinuclear subunits. For this reason we have interpreted the magnetic data according to the actual dinuclear nature of the complex through the spin Hamiltonian $\mathbf{H} = -J\mathbf{S}_1\mathbf{S}_2$. The fit of the experimental data to the appropriate susceptibility expression derived from the van Vleck formula and assuming that the *g* factors for both Cu(II) ions are identical, leads to J = -310(5) cm⁻¹ and g = 2.08(1). The observed *J* values lie in the upper range of the magnetic interactions found for related bis(μ -pyrazolato)-bridged dinuclear complexes. (Figure S6)

Fig.S6. Plot of $\chi_{\rm M}T$ vs. *T* for the complex 1.

The pathway for the magnetic exchange is propagated through the bridging pyrazolate ligands. From the molecular structure of **1**, one can conclude that the unpaired electron in each metal centre is clearly described by a d_{x-y}^{2-2} magnetic orbital which is coplanar with the pyrazolate skeleton. The significant overlap between these magnetic orbitals accounts for the strong antiferromagnetic coupling observed.

Magnetic Properties of hexanuclear copper(II) complexes 2.

Figure S7. Thermal dependence of χ_M and $\chi_M T$ for **2**. Solid line is the theoretical curve using the best-fit parameters (see text).