SHORT PAPER

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Synthesis and crystal structures of [Cu{HC(pz)$_3$}(SCN)$_2$] and [Cu(tacn)(SCN)$_2$] (HC(pz)$_3$: tris(pyrazolyl)methane; tacn: 1,4,7-triazacyclononane)[†]

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Two novel copper complexes with formulae [Cu{HC(pz)$_3$}(SCN)$_2$] **1** and [Cu(tacn)(SCN)$_2$] **2** have been obtained by the reaction of HC(pz)$_3$ and tacn with a copper salt and thiocyanate. The complex **1** crystallises in the orthorhombic space group A_{ba2}, with lattice parameters a = 25.7715(7) Å, b = 7.5034(3) Å, c = 16.2328(6) Å, Z = 8, R_1 = 0.0613, wR_2 = 0.1353. The complex **2** crystallises in the orthorhombic space group $P_{2(1)2(1)2(1)}$, with lattice parameters a = 8.640(4) Å, b = 10.890(5) Å, c = 13.833(6) Å, Z = 4, R_1 = 0.0343, wR_2 = 0.0679. Both complexes are isostructural mononuclear compounds. The central copper ions of **1** and **2** are coordinated by three nitrogen atoms of the ligands and two nitrogen atoms of the two thiocyanate ions. Depending on the ligands, the two complexes forms different weak bonds resulting in different crystal packing.

Keywords: [Cu{HC(pz)$_3$}SCN)$_2$], [Cu(tacn)(SCN)$_2$], copper (II) complex, crystal structure

Copper is at the centre of the active sites of many metalloenzymes and metalloproteins, for example hemocyanin (HC) and nitrite reductases (NiR). In such metalloenzymes and metalloproteins, each copper atom is coordinated by three nitrogen atoms of three imidazoles of histidines of proteins. Tris(pyrazolyl)methane and 1,4,7-triazacyclononane (tacn) are both tridentate ligands containing three nitrogen atoms which have strong coordinating ability. Current research in bioinorganic chemistry has shown that these two facially-coordinating tridentate ligands can mimic the tris(imidazole)binding sites of enzymes, provide protected binding pockets for small molecules, and control the nuclearity and reactivity pathways of metal centers.[1–3] The coordination chemistry of these two ligands has extensively been developed during the past several years. In this paper we present the synthesis, crystal structures and properties of two novel copper complexes, namely [Cu{HC(pz)$_3$}(SCN)$_2$] **(1)** and [Cu(tacn)(SCN)$_2$] **(2)** (HC(pz)$_3$: tris(pyrazolyl)methane; tacn: 1,4,7-triazacyclononane), and discuss their differences.

The ORTEP drawings of **1** and **2** are shown in Figs.1 and 2, respectively. Crystal data and structure refinements are summarised in Table 1. Selected bond lengths and angles are given in Table 2. Both are monomeric complexes, with similar coordination modes and molecular assembly order in the crystal. Each of the copper (II) ions is coordinated by five nitrogen atoms and one sulfur atom with a relatively weak coordination bond. In complexes **1** and **2**, the copper (II) ion is coordinated by three nitrogen atoms of the HC(pz)$_3$ or tacn ligand, respectively, and two nitrogen atoms from two thiocyanate molecules to form an approximate square pyramid. Four of the five nitrogen atoms lie almost in an approximately square plane, with the mean deviations from this plane of 0.1004 Å (for complex **1**) and 0.0042 Å (for complex **2**). In complex **1**, the bond Cu(1)-N(6) (2.570 Å) is longer than other Cu-N bonds. N(6) is at the top of the square pyramid. Since the angles N(8)–Cu–N(4) (170.7(4)°) and N(8)–Cu–N(4) (170.7(4)°) are close to 180°, Cu(1) can be seen as at the midpoint of the square plane. In complex **2,** Cu(1)–N(5) (2.268 Å)

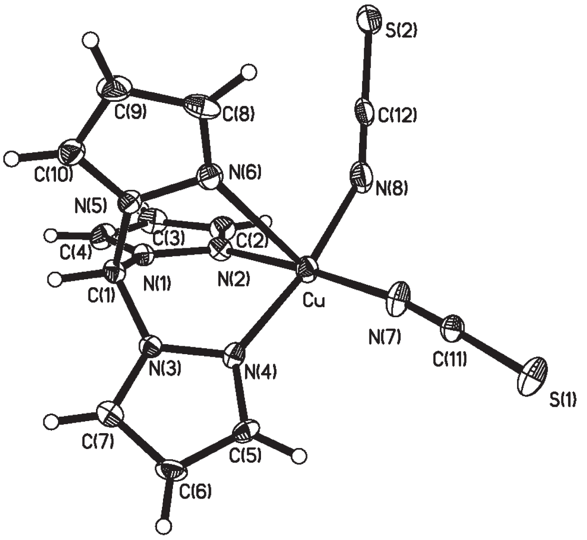

Fig. 1 The ORTEP drawing of [Cu{HC(pz)$_3$}(SCN)$_2$].

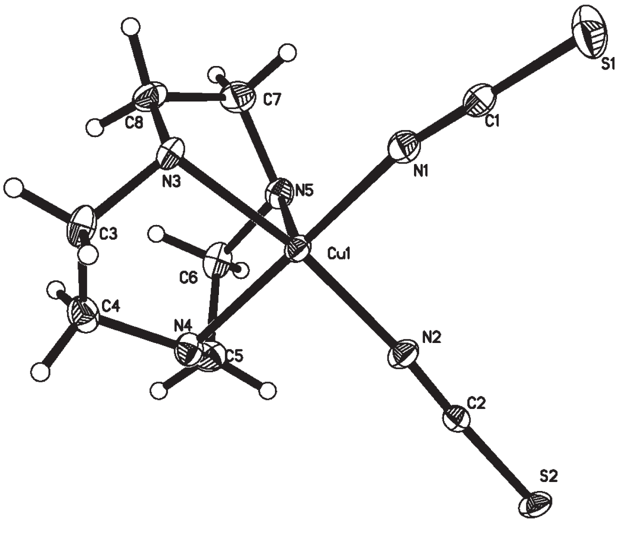

Fig. 2 The ORTEP drawing of [Cu(tacn)(SCN)$_2$].

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Data collection and processing parameters for **1** and **2**

	$[Cu\{HC(pz)_3\}(SCN)_2]$ (**1**)	[Cu(tacn)(SCN)2] (**2**)
Empirical formula	$C_9 H_{10} Cu N_{11} S_2$	$C_8 H_{12} Cu N_5 S_2$
Formula weight	399.94	305.89
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	A_{ba2}	$P_{2(1)2(1)2(1)}$
a (Å)	25.7715(7)	8.640(4)
b (Å)	7.5034(3)	10.890(5)
c (Å)	16.2328(6)	13.833(6)
β (°)	90	90
Volume	3139.00(19) Å^3	1301.5(10) Å^3
Z	8	4
Density (calculated) (mg/m^3)	1.693	1.561
Absorption coefficient(mm^{-1})	1.674	1.980
F(000)	1616	624
Crystal size (mm^3)	0.30 × 0.26 × 0.08	0.30 × 0.25 × 0.20
θ range for data collection (°)	1.58 - 25.11	2.38 - 25.03
Limiting indices	$-23 \le h \le 30$ $-8 \le k \le 8$ $-15 \le l \le 19$	$-10 \le h \le 9$ $-12 \le k \le 10$ $-9 \le l \le 16$
Reflections collected	5484	5378
Independent reflections	2551 [R(int) = 0.0496]	2297 [R(int) = 0.0389]
Absorption correction	Empirical	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6488	0.6929 and 0.5881
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2551 / 1 / 208	2297 / 0 / 145
Goodness-of-fit on F^2	1.373	1.054
*R*1, *wR*2 [I>2σ (I)]	0.0613, 0.1353	0.0343, 0.0679
*R*1, *wR*2 (all data)	0.0878, 0.1547	0.0475, 0.0717
Largest diff. peak and hole	0.414 and –0.469 e·Å^{-3}	0.419 and –0.317 e·Å^{-3}

^{a}R1 = $\Sigma\left|\,|F_o| - |F_C|\,\right|/\Sigma|F_o|$, wR2 = $(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2)^{1/2}$,. w = $1/[\sigma^2(Fo^2) + (0.0382P)^2 + 18.5943P]$, P = $(Fo^2+2Fc^2)/3$ for **1** and w = $1/[\sigma^2(Fo^2) + (0.0300P)^2 + 0.0000P]$, P = $(Fo^2 + 2Fc^2)/3$ for **2**.

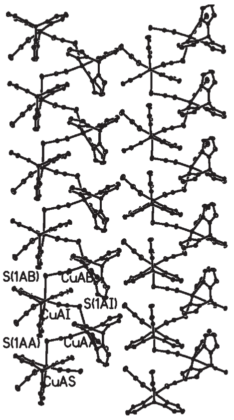

Fig. 3 The molecule packing of $[Cu\{HC(pz)_3\}(SCN)_2]$.

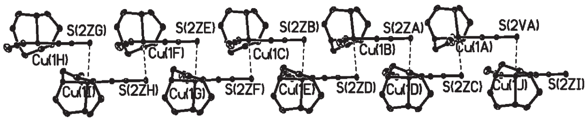

Fig. 4 The molecule packing of $[Cu(tacn)(SCN)_2]$.

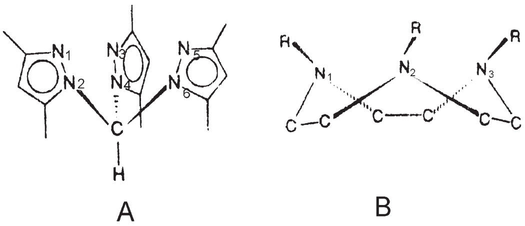

Fig. 5 Structures of the facially coordinating tridentate ligands discussed in this paper. **A**, $HC(pz)_3$ **B**, tacn.

Table 2 Selected bond lengths (Å) and angles (°) for (**1**) and (**2**)

$[Cu\{HC(pz)_3\}(SCN)_2]$ (**1**)		$[Cu(tacn)(SCN)_2]$ (**2**)	
Cu–N(7)	1.927(8)	Cu(1)–N(1)	1.975(5)
Cu–N(8)	1.978(10)	Cu(1)–N(2)	1.974(3)
Cu–N(4)	2.011(8)	Cu(1)–N(4)	2.050(4)
Cu–N(2)	2.017(7)	Cu(1)–N(3)	2.055(3)
Cu–N(6)	2.570(9)	Cu(1)–N(5)	2.268(3)
N(7)–Cu–N(8)	94.4(4)	N(1)–Cu(1)–N(2)	91.85(17)
N(7)–Cu–N(4)	91.2(4)	N(1)–Cu(1)–N(4)	175.39(15)
N(8)–Cu–N(4)	170.7(4)	N(2)–Cu(1)–N(4)	89.68(16)
N(7)–Cu–N(2)	175.5(4)	N(1)–Cu(1)–N(3)	94.92(15)
N(8)–Cu–N(2)	88.0(3)	N(2)–Cu(1)–N(3)	171.57(16)
N(4)–Cu–N(2)	86.9(3)	N(4)–Cu(1)–N(3)	83.19(15)
N(7)–Cu–N(6)	105.0(3)	N(1)–Cu(1)–N(5)	101.04(15)
N(8)–Cu–N(6)	92.2(4)	N(2)–Cu(1)–N(5)	100.40(14)
N(4)–Cu–N(6)	79.2(3)	N(4)–Cu(1)–N(5)	82.94(14)
N(2)–Cu–N(6)	78.7(3)	N(3)–Cu(1)–N(5)	83.24(13)

is longer than the other Cu-N bonds, and N(5) is the apex of the approximate square pyramid. Since the angles N(1)–Cu(1)–N(4) (175.39°) and N(2)–Cu(1)–N(3) (171.57°) are close to 180°, Cu(1) lies approximately in the center of the basal plane.

In both complexes, the pyramids are connected via a weak Cu–S bond (3.025 Å for **1,** 3.094 Å for **2**), where the copper ion and the sulfur atom are from different pyramids. Taking into account the weak coordination bond, both of the complexes can be considered as forming a one dimensional chain. (Figs.3 and 4)

Quantum-chemical calculations have been carried out at the DFT/B3LYP/6-31G level with the GAUSSIAN-94 set of routines for the experimental geometry of complex segment A, as found in the solid state. The results of the calculation are listed

Table 3 Atomic charges (Mulliken charges) of two ligands

Atom[HC(pz)$_3$]	N$_1$	N$_2$	N$_3$	N$_4$	N$_5$	N$_6$
A.C.	–0.490887	–0.139448	–0.489413	–0.132925	–0.490120	–0.144049
Atom [tacn]	N$_1$	N$_2$	N$_3$			
A.C.	–0.205299	–0.207330	–0.232201			

in Table 3 and the numbers of the atoms in the two ligands pictures are shown in Fig.5. From the calculated atomic charges, we can see that the N_1, N_3, N_5 atoms in ligand A have the highest electron donation. So HC(pz)$_3$ coordinates more strongly with central ions than tacn.

Experimental

Copper(II) perchloate hexahydrate, tacn and HC(pz)$_3$ were obtained by the methods described in the literature. [4-6] The two ligands have been characterised by Elemental analyses and NMR spectroscopy. Thiocyanate and other chemical reagents were obtained from commercial sources and used without further purification.

The complex **1** was prepared by using the H-tube method. HC(pz)$_3$ (0.2 mmol, 0.04286 g) was placed into one side of the H-tube, and then Cu(ClO$_4$)$_2$·6H$_2$O (0.2 mmol, 0.0748 g) and KSCN (0.6 mmol, 0.0583 g) was added to the other side of the H-tube, An ethanol–water(1:1) solution (10 ml) was slowly infused into the tube then the nozzle was sealed with tape. After about three weeks, green crystals of **1** suitable for X-ray analysis were obtained. Yield: 36%. Elemental analyses: found (%): C, 36.86, N, 29.34, H, 2.66. Calculated for $C_{12}H_{10}CuN_8S_2$ (%): C, 36.55, N, 29.51, H, 2.54.

The complex **2** was prepared by a different method. An methanol solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.2 mmol, 0.0748 g) was added to a methanol solution of tacn (0.2 mmol, 0.0258 g), then a methanol solution of NaSCN (0.2 mmol, 0.0162 g) was added to the mixed solution. After being stirred for 1 h at room temperature, the green solution was filtered and slowly evaporated in a refrigerator. After about one night, green crystals of **2** suitable for X-ray analysis were obtained. Yield: 50%. Elemental analyses: found (%): C, 39.80, N, 5.85, H, 5.58. Calculated for $C_8H_{12}CuN_5S_2$ (%): C, 40.05, N, 5.42, H, 5.84.

X-ray diffraction data were collected on a SIEMENS SMART CCD detector with graphite-monochromatised Mo-Kα radiation (λ = 0.71073 Å) for compound **1** and a BRUKER SMART 1000 CCD detector with graphite-monochromatised Mo-Kα radiation (λ = 0.71073 Å) for compound **2,** respectively. The structures have been solved by direct methods using the program SHELXS 97 [7] and Fourier difference techniques. Refinement has been by full-matrix least-squares method on F^2 using SHELXL 97. [8] Crystal data and structure refinements are summarised in Table 1. Selected bond lengths and angles are given in Table 2.

Infrared spectra (KBr pellets) were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–600 cm^{-1}. NMR spectra were recorded using a Mercury VX300M instrument. In the IR spectra, the typical stretching frequencies $\nu_{s(SCN)}$ are observed at 2100 cm^{-1} in both complexes. The IR spectra of the complex **1** confirms the existence of C–H bonds of HC(pz)$_3$ in the region 3125 cm^{-1}, C=C and C=N bonds in the region 1665–1430 cm^{-1}. The IR spectra of complex **2** confirms the existence of N-H bonds of tacn at 3250 cm^{-1} and 3100 cm^{-1}.

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