

# Novel binuclear copper(I) complexes with unusual azide and thiocyanate bridges. Crystal structures of $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}\cdot\text{Et}_2\text{O}$ and $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}\text{[Ph}_2\text{Ppyz} = 2\text{-}(\text{diphenylphosphino})\text{-6-(pyrazol-1-yl)pyridine}]$

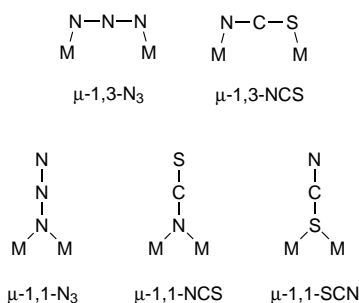
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The first binuclear copper(I) complex with a  $\mu\text{-1,1-N}_3$  bridge,  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}\cdot\text{Et}_2\text{O}$  and  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}\text{[Ph}_2\text{Ppyz} = 2\text{-}(\text{diphenylphosphino})\text{-6-(pyrazol-1-yl)pyridine}]$ , which exhibits an unusual thiocyanate ( $\mu\text{-1,1-SCN}$ ) bridge, have been synthesised and characterised.

The pseudo-halides  $\text{N}_3^-$  and  $\text{NCS}^-$  are known to co-ordinate to metals in both the terminal and bridging modes. As bridging ligands, they can link a pair of metal centres in either an end-on ( $\mu\text{-1,1}$ ) or a side-on ( $\mu\text{-1,3}$ ) bonded fashion (see below).



Binuclear copper azide systems are of considerable interest due to the broad range of their structural and magnetic properties, and they have been widely explored as structural models for copper-containing enzymes involved in the reversible binding and activation of dioxygen, *e.g.* hemocyanin.<sup>1</sup> However, the vast majority of studies have focused on binuclear copper(II) azide complexes.<sup>2</sup> On the other hand, reports on binuclear copper(I) complexes are scarce and only one structure, namely that of  $[(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-1,3-N}_3)\text{Cu}(\text{PPh}_3)_2]$  which exhibits a  $\mu\text{-1,3-N}_3$  bridge,<sup>3</sup> has been established. To our knowledge, there is as yet no known example of a binuclear copper(I) with a  $\mu\text{-1,1-N}_3$  bridge. We report here the first structure of this kind in the binuclear copper(I) complex  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}\cdot\text{Et}_2\text{O}$  [ $\text{Ph}_2\text{Ppyz} = 2\text{-}(\text{diphenylphosphino})\text{-6-(pyrazol-1-yl)pyridine}]$ .

Analogous binuclear copper thiocyanate complexes usually exhibit the  $\mu\text{-1,3-NCS}$  co-ordination mode.<sup>4</sup> Only one binuclear copper(I) compound with the  $\mu\text{-1,1-SCN}$  co-ordination mode, namely  $[\text{Cu}_2\text{L}(\mu\text{-1,1-SCN})_2]$  (L = macrocyclic Schiff base),<sup>5</sup> has been structurally characterised. Herein we describe a second example of this type in the binuclear copper(I) complex  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}$ .

We have recently prepared a new tridentate phosphine ligand, 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine ( $\text{Ph}_2\text{Ppyz}$ ) in two steps.<sup>6</sup> Reaction of  $\text{Ph}_2\text{PLi}$  (generated *in situ* from  $\text{Ph}_2\text{PH}$

and  $\text{LiBu}^n$ ), with 2,6-dichloropyridine at low temperature yielded the mono-substituted product 2-diphenylphosphino-6-chloropyridine, which in turn reacted with potassium pyrazolate to give  $\text{Ph}_2\text{Ppyz}$ . Reaction of  $\text{Ph}_2\text{Ppyz}$  with 1 equivalent of  $[\text{Cu}(\text{MeCN})_4]\text{[ClO}_4\text{]}$  resulted in the formation of  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\text{MeCN})_2]\text{[ClO}_4\text{]}_2$ ,<sup>6</sup> which reacted with  $\text{NaN}_3$  or  $\text{KSCN}$  in MeCN at room temperature to afford  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}$  **1** or  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}$  **2** in high yield.<sup>†</sup> Subsequent diffusion of  $\text{Et}_2\text{O}$  into their MeCN solutions gave crystals of **1**· $\text{Et}_2\text{O}$  or **2** suitable for X-ray crystallography.<sup>§</sup>

The IR spectrum of  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}\cdot\text{Et}_2\text{O}$  shows the characteristic asymmetric  $\text{N}_3$  stretching vibration at  $2037\text{ cm}^{-1}$ , which is in good agreement with the existence of the end-on bonded azide group, but a little lower than that (about  $2070\text{ cm}^{-1}$ ) of binuclear copper(II) complexes with a ( $\mu\text{-1,1-N}_3$ ) bridge.<sup>2c,d,7-9</sup> The IR spectrum of  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}$  shows the symmetric SCN stretching vibrations at 2091 (mainly CN) and  $693\text{ cm}^{-1}$  (mainly CS), which are comparable to those (2105 and  $700\text{ cm}^{-1}$ ) of the complex  $[\text{Cu}_2\text{L}(\mu\text{-1,1-SCN})_2]$  (L = macrocyclic Schiff base).<sup>5</sup> The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectra of **1**· $\text{Et}_2\text{O}$  and **2** show a singlet at  $\delta$  18.51 and 20.57, respectively.

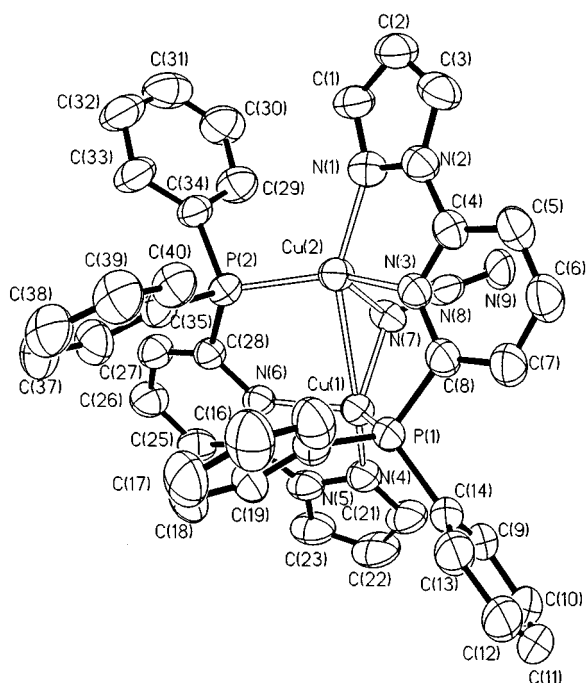
The molecular structure of the cation  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]^+$  in **1**· $\text{Et}_2\text{O}$  is depicted in Fig. 1. The two copper(I) centres are bridged by two  $\text{Ph}_2\text{Ppyz}$  ligands and a disordered  $\mu\text{-1,1-azide}$ § (see legend to Fig. 1). The geometry at each copper centre is highly distorted but, despite the large  $\text{N}(6)\text{-Cu}(1)\text{-P}(1)$  and  $\text{N}(3)\text{-Cu}(2)\text{-P}(2)$  angles of  $130.4(1)$  and  $139.9(1)^\circ$ , better described as a distorted square pyramid with the azide bridge in the axial position, rather than as a trigonal bipyramid. The  $\text{Cu}(1)\text{-Cu}(2)$  distance of  $2.773(1)\text{ \AA}$  is significantly shorter than

† Preparation of  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}\cdot\text{Et}_2\text{O}$  and  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}$ . Solid  $\text{NaN}_3$  or  $\text{KSCN}$  (0.30 mmol) was added to a solution of  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\text{MeCN})_2]\text{[ClO}_4\text{]}_2$  (0.32 g, 0.30 mmol) in MeCN (20 mL), and the mixture was stirred at room temperature for 48 h. Filtration followed by vapour diffusion of  $\text{Et}_2\text{O}$  into their concentrated solutions afforded yellow crystals. Complex **1**· $\text{Et}_2\text{O}$  (0.25 g, 83%): IR (KBr disc)  $\nu(\text{N}_3)$   $2037\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.63 (d,  $J = 0.6, 2\text{ H}$ ), 8.23 (m, 4 H), 7.34 (m, 20 H), 7.02 (m, 4 H), 6.63 (t,  $J = 0.6$ ), 3.45 (t,  $J = 0.4, 2\text{ H}$ ), 1.21 (t,  $J = 0.4\text{ Hz}, 3\text{ H}$ );  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR  $\delta$  18.51. Complex **2**: (0.23 g, 72%): IR (KBr disc)  $\nu(\text{SCN})$  2091,  $693\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.58 (d,  $J = 0.5, 2\text{ H}$ ), 8.17 (m, 4 H), 7.31 (m, 20 H), 7.07 (m, 4 H), 6.55 (t,  $J = 0.5\text{ Hz}$ );  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR  $\delta$  20.57.

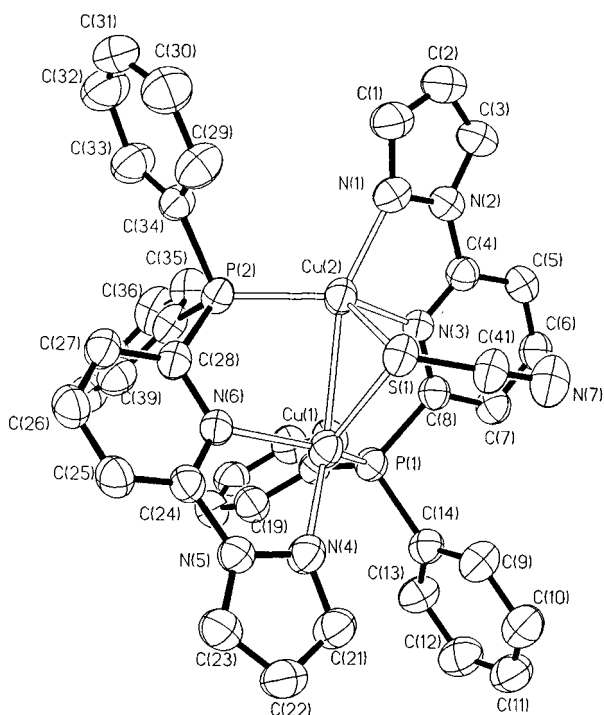
§ Crystal data.  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]\text{[ClO}_4\text{]}\cdot\text{Et}_2\text{O}$ ,  $\text{C}_{40}\text{H}_{32}\text{ClCu}_2\text{N}_9\text{O}_4\text{P}_2\cdot\text{Et}_2\text{O}$ ,  $M = 1001.34$ , monoclinic, space group  $P2_1/c$  (no. 13),  $a = 25.124(2)$ ,  $b = 12.824(1)$ ,  $c = 14.796(1)\text{ \AA}$ ,  $\beta = 104.62(10)^\circ$ ,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 1.104\text{ mm}^{-1}$ ; 6526 observed data [ $|F_o| > 4\sigma(F_o)$ ] out of 7305 unique reflections converged to  $R_F = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.064$  and  $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w|F_o|^2]\}^{1/2} = 0.079$ .

$[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]\text{[ClO}_4\text{]}$ ,  $\text{C}_{41}\text{H}_{32}\text{ClCu}_2\text{N}_7\text{O}_4\text{P}_2\text{S}$ ,  $M = 943.30$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 10.919(2)$ ,  $b = 13.535(3)$ ,  $c = 14.882(3)\text{ \AA}$ ,  $\alpha = 71.86(3)$ ,  $\beta = 83.06(3)$ ,  $\gamma = 87.94(3)^\circ$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 1.267\text{ mm}^{-1}$ ; 5604 observed data out of 6269 unique reflections converged to  $R_F = 0.054$  and  $R_w = 0.060$ . CCDC reference number 186/778.

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**Fig. 1** Perspective view (35% thermal ellipsoids) of the  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-N}_3)]^+$  cation in  $1 \cdot \text{Et}_2\text{O}$ . For clarity the disordered azide ligand is shown in only one of its two populated locations; dimensions relating to the N(7') atom of the alternative location are enclosed in square brackets. Pertinent bond lengths (Å) and angles ( $^\circ$ ): Cu(1)–Cu(2) 2.773(1), Cu(1)–P(1) 2.192(2), Cu(2)–P(2) 2.173(1), Cu(1)–N(7) 2.10(2) [2.09(2)], Cu(1)–N(4), 2.030(5), Cu(1)–N(6), 2.150(4), Cu(2)–N(7) 2.22(1) [1.93(1)], Cu(2)–N(1), 2.084(4), Cu(2)–N(3) 2.084(4); Cu(1)–N(7)–Cu(2) 79.8(4) [87.1(5)], N(7)–Cu(1)–Cu(2) 52.1(4), [44.1(4)], N(7)–Cu(2)–Cu(1) 48.1(4) [48.8(6)], N(6)–Cu(1)–P(1) 130.4(1), N(4)–Cu(1)–Cu(2) 152.4(2), N(1)–Cu(2)–Cu(1) 154.7(1), N(3)–Cu(2)–P(2) 139.9(1), N(4)–Cu(1)–N(6) 78.0(2), N(1)–Cu(2)–N(3) 78.5(2)



**Fig. 2** Perspective view (35% thermal ellipsoids) of the  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]^+$  cation in **2**. Pertinent bond lengths (Å) and angles ( $^\circ$ ): Cu(1)–Cu(2) 2.766(1), Cu(1)–S(1) 2.374(1), Cu(1)–N(4) 2.088(3), Cu(1)–N(6) 2.096(2), Cu(2)–S(1) 2.412(1), Cu(2)–N(1) 2.083(3), Cu(2)–N(3) 2.119(2); Cu(1)–S(1)–Cu(2) 70.6(1), S(1)–Cu(1)–Cu(2) 54.1(1), S(1)–Cu(2)–Cu(1) 55.3(1), N(6)–Cu(1)–P(1) 138.0(1), N(4)–Cu(1)–Cu(2) 159.9(1), N(1)–Cu(2)–Cu(1) 158.6(1), N(3)–Cu(2)–P(2) 135.6(1), N(4)–Cu(1)–N(6) 78.2(2), N(1)–Cu(2)–N(3) 78.0(2)

those of binuclear copper(II) complexes with  $\mu\text{-1,1-azide}$  bridges, which are usually over 3.0 Å.<sup>2,7–9</sup> Since the Cu...Cu distances of two independent cations in  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\text{MeCN})_2][\text{ClO}_4]_2$  are 3.625(1) and 3.587(1) Å,<sup>6</sup> the short Cu(1)–Cu(2) distance is mainly caused, not by the rigidity of the bridging phosphine ligand, but by the desire for both Cu<sup>I</sup> atoms to maximize  $\sigma$  bonding with the sp orbital of the azide ligand, which is indicated by the very acute angles N(7)–Cu(1)–Cu(2) {52.1(4) [44.1(4)]} and N(7)–Cu(2)–Cu(1) {48.1(4) [48.8(6)]}. This is the probable reason for the stabilisation of the Cu<sup>I</sup> state. The azide bridge angle Cu(1)–N(7)–Cu(2) is 79.8(4) [87.1(5)] $^\circ$ , and such a small angle has never been found in binuclear copper(II) complexes with  $\mu\text{-1,1-azide}$  bridges.<sup>2,7–9</sup> The Cu–N (pypz) bond lengths of 2.150(4) and 2.030(5) Å for Cu(1), and 2.084(4) and 2.084(4) Å for Cu(2) are typical for a copper(I) centre chelated by nitrogen heterocycles.<sup>10</sup> The N–Cu–N 'bite angles' of 78.0(2) for Cu(1) and 78.5(2) $^\circ$  for Cu(2) for the bidentate pyridylpyrazole fragments are usual for relatively rigid bidentate diamine ligands, and the values are very similar to that [78.9(3) $^\circ$ ] found in  $[\text{Cu}_2\text{L}'_2(\text{MeCN})_2][\text{PF}_6]_2$  [ $\text{L}' = 2,6\text{-bis}(5\text{-methylpyrazol-3-yl})\text{pyridine}$ ]<sup>11</sup> and those [78.9(2) and 78.6(2) $^\circ$ ] found in  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\text{MeCN})_2][\text{ClO}_4]_2$ .<sup>6</sup>

Fig. 2 shows a perspective drawing of the cation  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppyz})_2(\mu\text{-1,1-SCN})]^+$  in **2** with the atom numbering scheme. The molecular structure is very similar to that in  $1 \cdot \text{Et}_2\text{O}$  except that the  $\mu\text{-1,1-azide}$  bridge is replaced here by a  $\mu\text{-1,1-thiocyanate}$  bridge. The choice of sulfur rather than nitrogen as the bridge atom is presumably associated with the class b or 'soft' nature of Cu<sup>I</sup>. The bond length of 2.766(1) Å for Cu(1)–Cu(2) is similar to that in  $1 \cdot \text{Et}_2\text{O}$ , but shorter than that [2.796(8) Å] of  $[\text{Cu}_2\text{L}(\mu\text{-1,1-SCN})_2]$  (L = macrocyclic Schiff base).<sup>5</sup> The Cu–S distances of 2.374(1) and 2.412(1) Å are in good agreement with the corresponding distances [2.37(1) and 2.39(1) Å] in  $[\text{Cu}_2\text{L}(\mu\text{-1,1-SCN})_2]$ .<sup>5</sup> The Cu–S–Cu angle of 70.6(1) $^\circ$  is smaller than the azide angle in  $1 \cdot \text{Et}_2\text{O}$ , which is a consequence of the longer Cu–S distances compared to Cu–N.

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