Crystal Structure of (cyano-C)(1,10-phenanthroline-*N,N'*)(triphenylphosphane)copper(I)

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The title copper(I) complex crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 9.1932(18)$, $b = 9.1550(18)$, $c = 16.757(4)\text{\AA}$, $\alpha = 84.72(2)^\circ$, $\beta = 86.45(2)^\circ$, $\gamma = 65.20(2)^\circ$, $V = 1274.5(4)\text{\AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.386\text{ g/cm}^3$ and $T = 220(2)\text{K}$. The structure was refined to the final $R1 = 0.0491$ using all 4570 observed reflections. The complex is monomeric with a terminal cyano group C-coordinated to the copper atom. The solid-state structure consists of a distorted tetrahedron geometry around the copper with an N_2P donor set.

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The driving force for the development of new copper(I) complexes derives from their potential applications as catalysis as well as starting blocks in organic and coordination chemistry. Also, due to their potential applications in molecular electronics, triphenylphosphane copper(I) derivatives have been receiving attention.¹

In a previous paper we reported on the direct electrosynthesis of cyano copper(I) complexes and their derivatives by the galvanostatic dissolution of copper anode with concomitant reduction of malononitrile at a platinum cathode.² These syntheses showed a new way to prepare $[(N-N)\text{Cu}(\text{PPh}_3)\text{CN}]$ ($N-N = 2,2'$ -bipyridine, 1,10-phenanthroline) used as a starting block in the synthesis of heteronuclear bimetallic cyanide-bridged complexes.³ In this paper we report on the first crystal structure determination of $[\text{Cu}(\text{CN})(\text{phen})(\text{PPh}_3)]$.

The title complex was prepared by reacting 1.2 mmol of 1,10-phenanthroline dissolved in 10 ml of acetonitrile and 10 ml of acetonitrile containing $[\text{Cu}(\text{CN})(\text{PPh}_3)_2]_n$ (0.8 mmol) at room temperature. Some yellowish single crystals suitable for X-ray characterization were collected after a few days.

The structure was solved by direct methods and the positional and anisotropic displacement parameters of the non-hydrogen

atoms were refined by a least-squares calculation on F^2 . Hydrogen atom positions were found in the Fourier map and refined isotropically. A summary of crystal data along with further details of the structure determination and refinement are given in Table 1. The atomic coordinates along with their equivalent isotropic displacement parameters are presented in Table 2. A chemical diagram for the complex is represented in Fig. 1.

The complex is monomeric with a terminal cyano group C-coordinated to the copper atom. The molecular structure with the atom numbering scheme is depicted in Fig. 2. Selected bond lengths and angles are given in Table 3. The solid-state structure consists of a distorted tetrahedron geometry around the copper with an N_2P donor set. The deviation arises from the

Fig. 1 Chemical diagram for the complex.

Table 1 Crystal data and experimental details

Empirical formula	$\text{C}_{31}\text{H}_{23}\text{N}_3\text{PCu}$
Formula weight (g mol^{-1})	532.03
Temperature (K)	220(2)
Wavelength ($\text{\AA}$)	0.71073
Crystal system	triclinic
Space group, Z	$P\bar{1}$, 2
Unit cell dimensions	$a = 9.1932(18)\text{\AA}$ $\alpha = 84.72(2)^\circ$ $b = 9.1550(18)\text{\AA}$ $\beta = 86.45(2)^\circ$ $c = 16.757(4)\text{\AA}$ $\gamma = 65.20(2)^\circ$ $V = 1274.5(4)\text{\AA}^3$
Density _{calc.}	$D_x = 1.386\text{ g/cm}^3$
No. of reflections used	4570
θ_{max}	25.93° with Mo K_α
$R1(\text{all data})$	0.0363
$(\Delta\rho)_{\text{max}}$	$0.612\text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	$-0.912\text{ e\AA}^{-3}$
Measurement	STOE-IPDS
Program system	XStep32 (Stoe)
Structure determination	SHELX
Refinement	Full-matrix least-squares on F^2

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Table 2 Atomic coordinates ($\text{\AA} \times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
C(1)	2655(4)	2918(3)	723(2)	35(1)
C(2)	1807(4)	3376(4)	1053(2)	36(1)
C(3)	3077(4)	3199(4)	732(2)	44(1)
C(4)	2948(5)	1687(5)	629(2)	43(1)
C(5)	1511(4)	338(4)	837(2)	35(1)
C(6)	1227(5)	1292(5)	708(2)	43(1)
C(7)	182(5)	2543(4)	886(2)	45(1)
C(8)	1452(5)	2303(3)	1220(2)	38(1)
C(9)	2951(5)	3564(4)	1420(2)	48(1)
C(10)	4111(5)	3217(4)	1701(2)	52(1)
C(11)	3804(5)	1607(4)	1778(2)	44(1)
C(12)	1227(4)	717(3)	1339(2)	29(1)
C(13)	289(4)	621(3)	1152(2)	26(1)
C(14)	1915(4)	1024(3)	3639(2)	31(1)
C(15)	1035(4)	156(4)	3519(2)	40(1)
C(16)	1105(5)	1127(4)	4051(2)	51(1)
C(17)	2093(5)	1567(4)	4704(2)	51(1)
C(18)	2968(5)	724(4)	4834(2)	51(1)
C(19)	2891(5)	568(4)	4304(2)	41(1)
C(20)	64(4)	4423(3)	3234(2)	29(1)
C(21)	668(5)	5705(4)	2667(2)	46(1)
C(22)	1968(5)	7101(4)	2880(3)	57(1)
C(23)	2586(5)	7222(4)	3654(2)	53(1)
C(24)	1901(5)	5955(4)	4220(2)	48(1)
C(25)	565(4)	4564(4)	4016(2)	38(1)
C(26)	3517(4)	3032(3)	3079(2)	27(1)
C(27)	4974(4)	2048(4)	2736(2)	41(1)
C(28)	6357(5)	2254(5)	2840(2)	49(1)
C(29)	6282(5)	3478(5)	3284(2)	49(1)
C(30)	4838(5)	4480(5)	3622(2)	47(1)
C(31)	3451(5)	4268(4)	3526(2)	39(1)
N(1)	3188(4)	3340(4)	157(2)	50(1)
N(2)	435(3)	2135(3)	1271(1)	26(1)
N(3)	2398(3)	379(3)	1603(1)	32(1)
Cu	1712(1)	2113(1)	1625(1)	31(1)
P	1775(1)	2655(1)	2882(1)	28(1)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$$

geometrical constraints imposed by the bond angle N2-Cu-N3 of $80.41(10)^\circ$, which differs significantly from the ideal value of 109.5° . That the steric bulk of PPh_3 and phen ligands compare to the cyano group is explained by the N2-Cu-P and N3-Cu-P angles of $116.25(7)^\circ$ and $108.22(7)^\circ$ compared to $111.07(11)^\circ$ and $108.68(11)^\circ$ for the C1-Cu-N3 and C1-Cu-N2 and $123.78(9)^\circ$ for C1-Cu-P angles.

The cyano group is almost linear (Cu-C1-N1 $175.70(3)^\circ$). The Cu-P distance of $2.218(9)\text{\AA}$ and the Cu-N distances of $2.087(2)$ and $2.100(2)\text{\AA}$ are in good agreement with the literature.⁴ Also, the value of the C1-N1 bond length of $1.150(4)\text{\AA}$ is closely compared with that expected for a terminal CN triple bond.⁴

Table 3 Selected bond distances and angles

Cu-C1	1.935(4)	C1-Cu-P	123.78(9)
Cu-N2	2.087(2)	N2-Cu-P	116.25(7)
Cu-N3	2.100(2)	N3-Cu-P	108.22(7)
Cu-P	2.218(9)	N2-Cu-N3	80.41(10)
C1-N1	1.150(4)	N1-C1-Cu	175.70(3)
		C1-Cu-N2	108.68(11)
		C1-Cu-N3	111.07(11)

Fig. 2 Perspective view of the molecular structure of $[\text{Cu}(\text{CN})(\text{phen})(\text{PPh}_3)]$, showing the thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity).

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