

[Cu(CN)en₂]I – Copper Amine Propellers

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

Light blue [Cu(CN)en₂]I was prepared by reaction of copper iodide with ethylenediamine (*en*) and potassium cyanide in acetonitrile in air. It crystallizes in the space group C₂ (No. 5) with $a = 11.082(6)$, $b = 7.155(2)$, $c = 9.017(3)$ Å, $\beta = 127.00(3)^\circ$, and $Z = 2$. The structure was refined from 1069 unique reflections and 90 parameters. The refinement converged to $R1 = 0.018$ and $wR2 = 0.041$ (all reflections). Copper has a trigonal bi-pyramidal environment formed by two *en* molecules and one CN[−] anion. The iodine anion shows no direct contact to the Cu²⁺ center. The propeller shaped complexes [Cu(CN)en₂]⁺ are all oriented parallel in the crystal structure. [Cu(CN)en₂]⁺ cations and I[−] anions form a zincblende related arrangement.

Key words: Copper (II) Complexes, Amines, Cyanide

Introduction

The use of copper(I) halides as a preparative tool for the synthesis of molecular units of main group elements has been established in the past decade [1]. These investigations were encouraged by earlier work of Rabenau *et al.* [2–4] and Möller and Jeitschko [5]. Trying to extract the copper halide matrix from the adducts and thus to separate the embedded molecular fragments after the high temperature synthesis we used

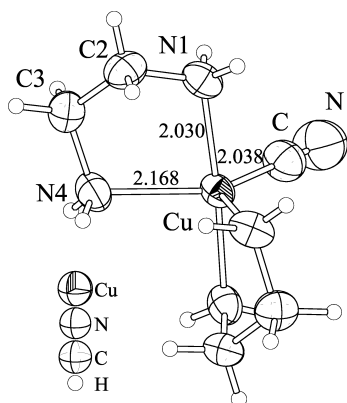


Fig. 1. Copper is coordinated in a trigonal bi-pyramidal manner by two *en*-molecules and one cyanide ion, the second *en* ligand is generated by symmetry. Displacement ellipsoids are drawn at the 80% probability level for all non-hydrogen atoms. Selected distances are given in Å.

different ligands such as cyanide and numerous amines, both in aqueous solution and inorganic solvents. Thus, copper is intended to be extracted from the solid compounds by forming soluble complexes. The insoluble molecular units remain unchanged at least in the cases of polymeric main group units [6]. Various complexes of copper(II) with amines and cyanide ions are known and well characterized. Therein, copper(II) as central atom has a distorted octahedral coordination sphere of amine nitrogen atoms and the carbon or nitrogen atoms of the cyanide ligands. In addition a limited number of trigonal bi-pyramidal complexes are known. Here, we report on the synthesis and characterization of [Cu(CN)en₂]I which was obtained during the above mentioned extraction experiments. The basic building unit is a propeller shaped [Cu(CN)en₂]⁺ complex.

Structure Determination and Discussion

Copper(II) is coordinated by two *en* molecules and one cyanide ion resulting in a [Cu(CN)en₂]⁺ complex. The ligands form a trigonal bi-pyramidal environment, see Fig. 1. Cu and the CN[−] ligand are located on a twofold axis, and the second amine ligand is generated by this twofold axis along [010]. The complex has the point group symmetry C₂. The coordination polyhedron has the shape of a propeller as shown in Fig. 1. Copper and the cyanide ligand form the shaft and the two amines are the blades. This moi-

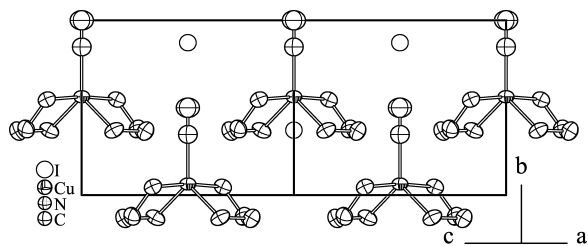


Fig. 2a. Section of the crystal structure of [Cu(CN)en₂]I, view along [101]. The dipole moments of the copper amine propellers are orientated along the *b*-axis. Hydrogen atoms are omitted for clarity.

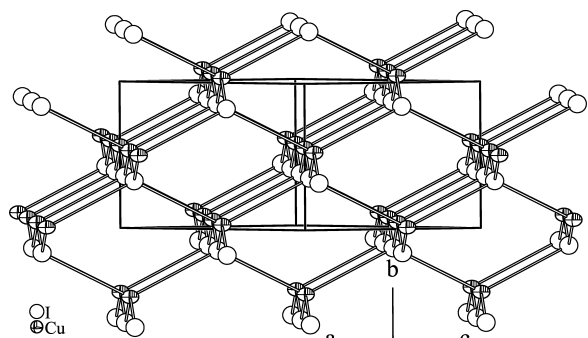


Fig. 2b. Copper and iodine atoms show the motif of a zincblende type structure. Distances between copper and iodine are about 5 Å.

ety is known from other compounds [10], but was not yet obtained as an isolated complex. The example given in [10] displays CN⁻ as a bridging ligand with the nitrogen atom coordinating Cu and the carbon atom coordinating Re. In addition the bond angle on the central N atom is about 150°, *i.e.*, the propeller shows some significant distortion. The distance $d(\text{Cu}-\text{C})$ is 2.038(8) Å, which is in the typical range for bonds between cyanide C atoms and copper(II). The Cu-N distances are $d(\text{Cu}-\text{N}1) = 2.030(3)$ and $d(\text{Cu}-\text{N}4) = 2.168(3)$ Å with the former one being rather short for copper(II) amine N bonds. The dipole moments of the copper propellers are all oriented parallel along the *b* axis, see Fig. 2a. This is the result of the missing center of symmetry in the crystal structure. The centers of the [Cu(CN)en₂]⁺ complexes and the iodine ions are arranged in a zincblende type structure, see Fig. 2b, which crystallizes also in a non-centrosymmetric structure.

Experimental Section

The title compound was first obtained as a by-product from the extraction reaction of (CuI)₃P₁₂ with *en* in acetonitrile.

Table 1. Crystallographic data and structure refinement for [Cu(CN)en₂]I.

Compound	CuCN(C ₂ N ₂ H ₈) ₂ I
Formula weight [g mol ⁻¹]	336.67
Crystal size [mm ³], color	0.1 × 0.1 × 0.05, light blue
Crystal system	monoclinic
Space group	C2 (No. 5)
Lattice constants in Å from powder diffraction	$a = 11.082(6)$ $b = 7.155(2)$ $c = 9.017(3)$ $\beta = 127.00(3)^\circ$
Cell volume, <i>Z</i>	571.0(4) Å ³ , 2
ρ_{calc} [g cm ⁻³]	1.958
Diffractometer	STOE IPDS I, Mo-K α , $\lambda = 0.71073$ Å, oriented graphite monochromator
Absorption correction	Numerical, crystal description with 10 faces
Temperature [°C]	-100
θ Range [°]	$2.83 \leq \theta \leq 25.67$
<i>hkl</i> Range	$-13 \leq h \leq +13$ $-8 \leq k \leq +8$ $-10 \leq l \leq +10$
No. of reflections	3921
No. of independent reflections, <i>R</i> _{int}	1069, 0.0385
No. of parameters	90
Structure solution	SIR92 [9]
Refinement	SHELX 97 [13]
Inversion twin ratio	0.19(3)
Final <i>R</i> / <i>wR</i> ($I > 2\sigma$, 1068 reflections)	0.0180/0.0430
Final <i>R</i> / <i>wR</i> (all 1069 reflections)	0.0180/0.0430
Goof	1.099
Largest difference maximum $\Delta\rho_{\text{max}}$ and minimum $\Delta\rho_{\text{min}}$ /(e Å ⁻³)	0.924 -0.484

Crystallographic data for the structure(s) have been deposited with the Cambridge Crystallographic Data Centre, CCDC-297149. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code+(1223)336-033; E-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} in Å² for [Cu(CN)en₂]I.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
I	2 <i>b</i>	0	0.8718	1/2	0.022(1)
Cu	2 <i>a</i>	0	0.5632(1)	0	0.018(1)
N	2 <i>a</i>	0	0.9993(9)	0	0.044(1)
C	2 <i>a</i>	0	0.848(1)	0	0.029(1)
N(1)	4 <i>c</i>	0.8854(3)	0.5462(4)	0.7207(3)	0.023(1)
C(2)	4 <i>c</i>	0.9344(3)	0.3792(6)	0.6725(4)	0.026(1)
C(3)	4 <i>c</i>	1.1075(3)	0.3664(8)	0.8057(4)	0.027(1)
N(4)	4 <i>c</i>	1.1493(2)	0.3708(5)	0.9963(3)	0.024(1)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

trile. Then the synthesis was optimized as follows: Copper iodide (Fluka, 99.99%) is dissolved in acetonitrile (Riedel de

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I	0.017(1)	0.024(1)	0.020(1)	0	0.009(1)	0
Cu	0.018(1)	0.013(1)	0.018(1)	0	0.009(1)	0
N	0.058(3)	0.033(2)	0.043(2)	0	0.031(2)	0
C	0.026(2)	0.030(4)	0.026(2)	0	0.014(1)	0
N1	0.020(1)	0.020(1)	0.023(1)	0.003(1)	0.010(1)	-0.001(1)
C2	0.025(1)	0.029(1)	0.020(1)	-0.006(1)	0.012(1)	-0.005(2)
C3	0.026(1)	0.028(2)	0.027(1)	-0.001(2)	0.017(1)	0.004(2)
N4	0.022(1)	0.022(1)	0.022(1)	-0.002(1)	0.009(1)	0.004(2)

Table 3. Anisotropic displacement parameters U_{ij} in Å² for [Cu(CN)*en*₂]I.Table 4. Hydrogen coordinates and isotropic displacement parameters U_{eq} in Å² for [Cu(CN)*en*₂]I.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
H(11)	4c	0.904(4)	0.634(6)	0.684(4)	0.08(9)
H(12)	4c	0.789(5)	0.541(6)	0.664(6)	0.2(1)
H(22)	4c	0.901(4)	0.388(7)	0.552(5)	0.27(8)
H(23)	4c	0.883(4)	0.280(7)	0.685(5)	0.20(9)
H(32)	4c	1.163(6)	0.47(1)	0.794(9)	0.5(2)
H(31)	4c	1.132(4)	0.247(5)	0.772(5)	0.06(8)
H(41)	4c	1.238(5)	0.397(8)	1.067(5)	0.4(1)
H(42)	4c	1.131(4)	0.251(6)	1.028(6)	0.3(1)

Table 5. Selected bond lengths in Å and angles in ° for [Cu(CN)*en*₂]I.

Cu-C		2.038(8)	Cu-N1	2×	2.030(3)
Cu-N4	2×	2.168(3)	C-N		1.008(1)
Cu-C-N		180	N1-Cu-N1 ⁱ		173.1(2)
C-Cu-N4		129.4(1)	N4-Cu-N4 ⁱ		101.1(2)
N1-Cu-N4		81.7(1)			

Symmetry transformations used to generate equivalent atoms:
ⁱ: $-x+2, y, -z+2$.

Haën, 99.5%) and one equivalent of solid potassium cyanide (99% Merck) is added. To the clear colorless solution *en* (99% Merck) is added drop wise until no further violet precipitate is observed. Then the fine, dark blue to violet powder is dissolved in a mixture of acetonitrile and ethanol (1 : 1). Additional acetonitrile is added to the filtered blue solution until it contains almost twice as much acetonitrile as ethanol. Then the solution is allowed to evaporate in an open flask. Two types of crystals form after two to three days. Dark violet octahedra of Cu*en*₂I₂ [11, 12] and light blue plates of the title compound [Cu(CN)*en*₂]I can be isolated. It can be assumed that Cu⁺ is oxidized by oxygen to Cu²⁺.

Single crystals were selected under a microscope, mounted on a glass fiber and checked for their quality by Weissenberg photographs. X-ray diffraction data of a light blue platelet of [Cu(CN)*en*₂]I were measured at 170 K on a STOE IPDS I, see Table 1 for details. Data were corrected

numerically for absorption after deriving an idealized description of the crystal shape with ten faces by X-SHAPE [7]. Extinction conditions allowed the space groups *C2*, *Cm*, and *C2/m*. A satisfying solution of the crystal structure was possible only in space group *C2* (No. 5). This was confirmed by the subsequent refinement. Tests for a higher symmetry failed [8]. Unit cell parameters from powder data were used: $a = 11.082(6)$, $b = 7.155(2)$, $c = 9.017(3)$ Å, $\beta = 127.00(3)^\circ$. Structure solution with direct methods [9] revealed the positions of one iodine, one copper, three carbon, and three nitrogen atoms. These non hydrogen atoms were refined with anisotropic displacement parameters. The *y* parameter of I had to be fixed to define the origin of the structure. By Difference Fourier syntheses all eight hydrogen atoms were located. They were refined with isotropic displacement parameters and without any restrictions. The refinement including twinning by inversion converged to $R1 = 0.018$ and $wR2 = 0.041$ for all reflections and 90 refined parameters, see Table 1. The refinement results are summarized in Tables 2–4, selected interatomic distances and angles are given in Table 5.

X-ray powder patterns were recorded at room temperature on a STOE STADI P diffractometer (Cu-K α_1 radiation, Ge(111) monochromator).

The decomposition temperature of [Cu(CN)*en*₂]I was determined by thermogravimetric measurements in streaming argon on a METTLER TG50. The heating rate was 5 °C min⁻¹. Decomposition of the title compound starts at 240 °C.

IR(KBr): $\tilde{\nu}(\text{C}\equiv\text{N}) = 2131 \text{ cm}^{-1}$. Elemental analysis: [Cu(CN)*en*₂]I (336.67): calcd. C 17.8, H 4.8, N 20.8; found C 19.4, H 3.1, N 22.3.

UV spectroscopy: one broad band with a maximum at ca. 15 000 cm⁻¹.

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