Notes

Synthesis and crystal structure of chain $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]_\infty$

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The chain $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]_\infty$ has been synthesized and characterized by X-ray crystallography. It crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 0.9985(2)$ nm, $b = 1.0998(2)$ nm, $c = 1.5174(2)$ nm, $\alpha = 87.89(1)°$, $\beta = 76.73(1)°$, $\gamma = 77.77(1)°$, $V = 1.5849(5)$ nm^3, $Z = 2$, $D_c = 2.095$ g/cm^3. $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]_\infty$ has a dimmer unit $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]$. The two N atoms of the phenyl ring of 2-aminopyrimidine bridge two $[CuI(PPh_3)]_2$ units, by which a one-dimensional chain is constructed. The van der Waals force makes the molecules arrange in the three-dimensional space.

Keywords Cu^I complex, 2-aminopyrimidine, triphenylphosphine

Introduction

The spectroscopic properties of complexes including 2-aminopyrimidine ligand have been studied for a long time.[1,2] Since the crystal structure of the first cobalt complex of 2-aminopyrimidine was determined in 1978,[3] the first Cu^{II} complex $[Cu(AMP)SO_4]\cdot 3H_2O$[4] and the first chain $[\{Cu_2(AMP)(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$[5] were determined. After then the crystal structure, IR spectra, magnetic properties, reflection spectra and thermal properties of Cu^{II} complexes have been studied extensively. But up to now, the crystal structure of Cu^I complex has not been reported. This may be due to the difficulty of the synthesis of Cu^I complexes resulting from their low solubility in the organic solvents and their unstability. We succeeded in synthesizing a series of Cu^I complexes $[CuX(PPh_3)L]_n$ [$n = 1$, X = I, L = 1,10-phen; $n = 2$, X = Br, I, L = C_9H_7N],[6-8] with nitrogen heterocycle complexes, halogen and triphenylphosphine as ligands. Here we report the synthesis and the crystal structure of a novel chain $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]_\infty$ (**1**) and compare it with other similar compounds.

Experimental

Instruments and reagents

Elemental analysis was conducted using a Perkin-Elmer 2400 element instrument. The IR spectra were characterized by a Perkin-Elmer 2000 FT-IR instrument. The crystal structure was determined by a DPI2030k area-detector refractometer.

All reagents were commercial products with analytical grade.

Synthesis

CuI (0.19 g, 1 mmol), PPh_3 (0.26 g, 1 mmol) and $C_4H_5N_3$ (0.10 g, 1 mmol) reacted in CH_2Cl_2 (20 mL) solution at room temperature for 6 hours. The solution was filtrated. The yellow crystals were obtained from slowly evaporating the solution. Anal. $Cu_2C_{44}H_{40}N_6I_2P_2$. Calcd: C, 47.93; H, 3.40; N, 4.10. Found: C, 47.95; H, 3.49; N, 4.19.

Structural determination

A block of yellow crystal **1** with approximate dimensions of 0.20mm × 0.20mm × 0.20mm was used for X-ray diffraction study. Data collection was performed on a

Received January 17, 2000; accepted June 27, 2000.
Project (No. 952871800) supported by Beijing Talent Found for Young Sci-Tech Researchers.

DPI2030k area-detector refractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.0710069$ nm) using ω scan mode. Unique 4472 reflections were collected. An empirical absorption correction based on Ψ-scan method was applied. The structure was solved by heavy atom method using Paterson analysis and Shelex93 program package. The structure was refined by full-matrix least-squares techniques for 3524 reflections with $I \geq (2.5\sigma(I)$ to final $R = 0.085$, $R_w = 0.082$, $(\Delta/\sigma)_{max} = 0.052$. Final difference Fourier maps showed that the highest and lowest electron densities are 980 and -1720 e/nm^3 respectively.

Crystal data: Space group $P\bar{1}$, $a = 0.9985(2)$ nm, $b = 1.0998(2)$ nm, $c = 1.5174(2)$ nm, $\alpha = 87.89(1)°$, $\beta = 76.73(1)°$, $\gamma = 77.77(1)°$, $V = 1.5849(5)$ nm^3, $Z = 2$, $D_c = 2.095$ g/cm^3, $R = 0.085$, $F(000) = 639.92$.

Result and discussion

Fig. 1 and Fig. 2 show that the title complex has a dimmer unit $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]$. The two N atoms of the phenyl ring of 2-aminopyrimidine bridge two $[CuI(PPh_3)]_2$ units, by which a one-dimensional chain is constructed. The molecules are arranged in the three-dimensional space by van der Waals force.

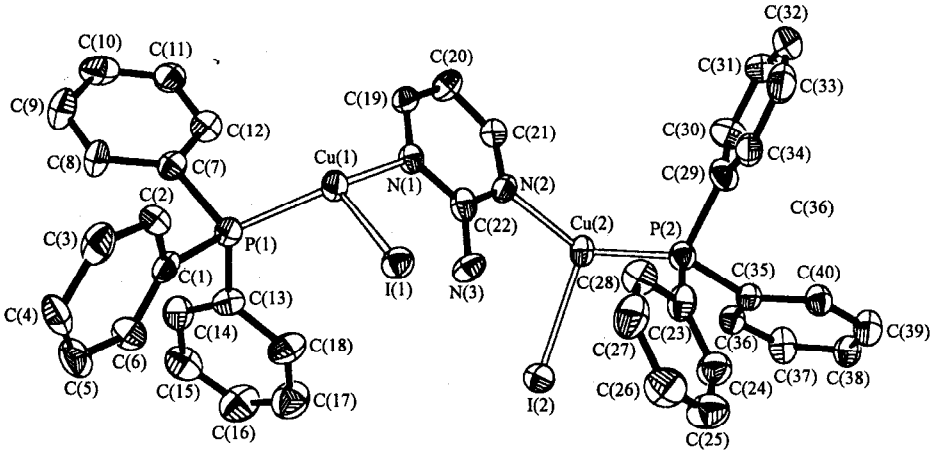

Fig. 1 Structure of complex **1**.

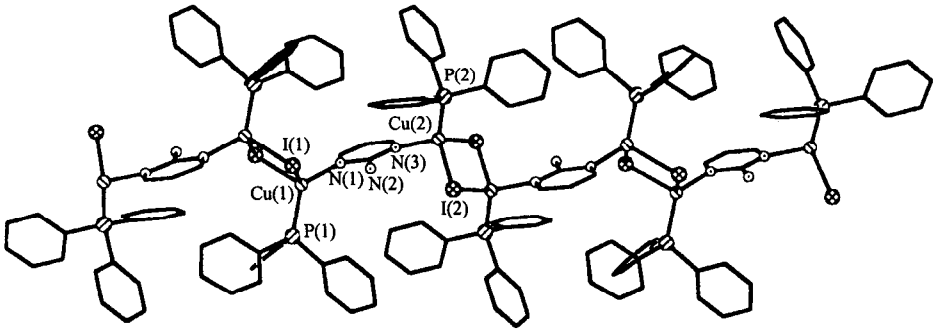

Fig. 2 Molecular packing of complex **1**.

In the unit $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]$ of the complex **1**, the Cu atom is in the center of the distorted coordination tetrahedron. Each Cu atom coordinates with one P atom of PPh_3, two I atoms, and one N atom of the phenyl ring in $C_4H_5N_3$. As a result of the coordination of N atom with 2-aminopyrimidine, the electric charge of 2-aminopyrimidine is transferred, and 2-aminopyrimidine molecules are isomerized to carbamamidine structure.

The bond lengths and bond angles are listed in Table 1. Compared with the chain $[Cu_2(\mu\text{-}4,4'\text{-bpy})_2(PPh_3)_2Cl]$ (bpy = bipyridine) (**2**)[9] and $[Cu(\mu_2\text{-Pz})$-

$(PPh_3)_2Cl)]$ (Pz = Pyrazine) (**3**),[10] the Cu···Cu distance of **1** is very close to that of **2** and **3**. But the Cu—N distances of complex **1** are slightly shorter than those of **2** and **3**. The Cu—N bond lengths of **1** are obviously shorter than those of the binuclear Cu^{II} complex $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4(C_4H_5N_3)\}_n]$ (**4**),[5] which also has a bidental ligand of 2-aminopyrimidine. The Cu—N bond lengths of **1** are obviously shorter than those of the binuclear Cu^{II} complex $[Cu_2(PCIBA)_4(C_4H_5N_3)]$ (**5**)[11] (PCIBA = *p*-chlorobenzeneoxyiosbutyl). This is because of the different valences of Cu atoms in **1**, **4** and **5**.

Table 1 Selected bond lengths [nm] and angles [°]

I(1)—Cu(1)	0.2510(2)	Cu(1)-I(1)-Cu(1)i	75.30(8)
I(1)—Cu(1)i	0.2559(2)	Cu(2)-I(2)-Cu(2)i	71.51(8)
I(2)—Cu(2)	0.2565(3)	I(1)-Cu(1)-I(1)i	104.70(9)
I(2)—Cu(2)i	0.2499(3)	I(1)-Cu(1)-P(1)	111.68(15)
Cu(1)—N(1)	0.1942(12)	I(1)i-Cu(1)-P(1)	105.22(15)
Cu(2)—N(2)	0.1978(13)	I(1)-Cu(1)-N(1)	110.4(4)
Cu(1)—P(1)	0.2094(5)	I(1)i-Cu(1)-N(1)	100.2(4)
Cu(2)—P(2)	0.2094(5)	P(1)-Cu(1)-N(1)	122.4(4)
Cu(1)···Cu(1)I	0.3097	I(2)-Cu(2)-I(2)i	108.49(9)
Cu(2)···Cu(2)I	0.2958	I(2)-Cu(2)-P(2)	104.11(16)
		I(2)-Cu(2)-N(2)	109.4(4)
		I(2)i-Cu(2)-P(2)	115.18(16)
		I(2)i-Cu(2)-N(2)	99.8(4)
		P(2)-Cu(2)-N(2)	119.5(4)

Table 2 Atomic coordinates and their thermal parameters

Atom	*x*	*y*	*z*	Biso
I(1)	0.0870(1)	0.1383(1)	0.4381(1)	4.4(1)
I(2)	0.1560(1)	0.0859(1)	0.0174(1)	5.0(1)
Cu(1)	0.0749(2)	-0.0838(1)	0.4158(1)	4.2(1)
Cu(2)	-0.0953(2)	0.0569(1)	0.0845(1)	4.4(1)
P(1)	0.2695(5)	-0.2046(4)	0.4104(3)	4.0(1)
P(2)	-0.2173(5)	0.2381(4)	0.0960(3)	4.3(2)
N(1)	-0.0390(13)	-0.0942(11)	0.3296(8)	3.6(6)
N(2)	-0.0971(14)	-0.0477(11)	0.1935(9)	4.1(6)
N(3)	0.0491(16)	0.0478(12)	0.2422(9)	4.7(7)
C(1)	0.3640(18)	-0.1671(14)	0.4821(11)	4.3(8)
C(2)	0.2921(16)	-0.1365(16)	0.5659(12)	4.5(8)
C(3)	0.3613(22)	-0.1114(17)	0.6274(12)	5.5(10)
C(4)	0.4957(18)	-0.1125(16)	0.6050(15)	5.5(10)
C(5)	0.5614(18)	-0.1409(17)	0.5197(16)	6.1(11)
C(6)	0.4968(18)	-0.1674(16)	0.4582(12)	4.8(8)
C(7)	0.2513(17)	-0.3538(14)	0.4411(11)	3.9(8)
C(8)	0.3222(20)	-0.4172(15)	0.4973(13)	5.0(9)
C(9)	0.3020(24)	-0.5301(18)	0.5143(15)	6.9(12)
C(10)	0.2158(21)	-0.5763(16)	0.4798(16)	6.3(11)
C(11)	0.1458(18)	-0.5103(17)	0.4282(13)	5.4(9)
C(12)	0.1674(19)	-0.3994(15)	0.4066(12)	4.7(9)
C(13)	0.3912(19)	-0.2293(16)	0.3112(13)	5.0(9)
C(14)	0.4839(19)	-0.3300(16)	0.2870(13)	5.2(9)
C(15)	0.5724(21)	-0.3420(19)	0.2102(15)	6.4(11)
C(16)	0.5670(30)	-0.2562(21)	0.1509(15)	7.3(13)

Continued

Atom	x	y	z	Biso
C(17)	0.4800(30)	-0.1477(22)	0.1739(16)	7.6(13)
C(18)	0.3912(22)	-0.1367(18)	0.2520(13)	6.0(11)
C(19)	-0.1143(16)	-0.1737(14)	0.3394(11)	4.2(7)
C(20)	-0.1808(20)	-0.1927(17)	0.2797(12)	5.2(10)
C(21)	-0.1652(17)	-0.1267(15)	0.2068(12)	4.6(8)
C(22)	-0.0303(18)	-0.0312(16)	0.2529(11)	4.5(8)
C(23)	-0.1542(20)	0.3386(16)	0.1490(12)	4.9(9)
C(24)	-0.0979(21)	0.4298(19)	0.1096(14)	5.9(10)
C(25)	-0.0407(24)	0.4998(21)	0.1529(15)	6.9(12)
C(26)	-0.0347(24)	0.4793(21)	0.2356(16)	7.0(12)
C(27)	-0.0910(30)	0.3877(20)	0.2754(15)	7.0(12)
C(28)	-0.1471(21)	0.3186(17)	0.2334(13)	5.6(10)
C(29)	-0.3882(17)	0.2533(16)	0.1494(12)	4.9(8)
C(30)	-0.4572(20)	0.1864(19)	0.1223(14)	5.8(10)
C(31)	-0.5953(21)	0.1944(21)	0.1622(18)	7.6(13)
C(32)	-0.6544(20)	0.2675(19)	0.2298(16)	7.0(11)
C(33)	-0.5834(22)	0.3321(19)	0.2591(14)	6.6(11)
C(34)	-0.4523(18)	0.3273(16)	0.2218(12)	5.1(9)
C(35)	-0.2334(17)	0.3100(15)	-0.0036(12)	4.3(8)
C(36)	-0.1729(17)	0.2493(15)	-0.0797(11)	4.2(7)
C(37)	-0.1938(21)	0.3009(17)	-0.1590(13)	5.6(10)
C(38)	-0.2686(20)	0.4125(17)	-0.1579(12)	5.3(9)
C(39)	-0.3314(21)	0.4723(18)	-0.0812(13)	5.7(10)
C(40)	-0.3147(18)	0.4219(16)	-0.0040(12)	4.6(8)

Biso is the mean of the principal axes of the thermal ellipsoid.

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(E200001011 JIANG, X.H.; DONG, L.J.)