Notes

Synthesis and Crystal Structure of Bis(Trialkylphosphine)(Bipyrimidine) Copper(I) Complexes

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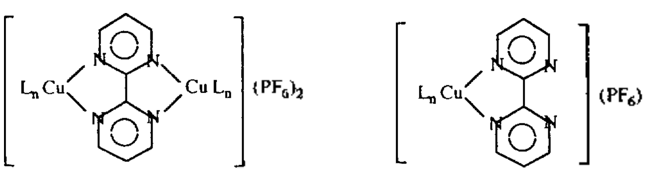
There has been considerable interest in the synthesis and characterization of metal complexes containing novel nitrogen aromatic heterocyclic ligands[1]. Ligands with multiple nitrogen sites that are μ-coordinating are utilized in the formation of bi- and polymetallic metal-ligand complexes[2], with application as electron-transfer processes[3] and metal-metal interactions[4]. The selection of bridging ligand can change the nature of metal-metal interaction. Bidentate coordination of ligand is desirable because of the chelate effect on complex stability and enhanced metal dπ-bridging ligand pπ-metal dπ electron interaction. 2,2'-Bipyrimidine (bpm) is known to act as a bridging ligand[5]. Recently, homo and heterobimetallic complexes of bpm including derivatives of Ru[6], Os[7], Pt[8], Re[9] and Cu[10] have been reported. In particular, copper(I) coordination chemistry is receiving much attention due mainly to the role of the metal in biological systems[11]. On view of the importance of copper(I) chemistry, we have initiated the reaction of Cu(I) complex and bpm in an attempt to obtain bimetallic transition metal complexes. (Chart I).



The Cu(II)-bpm system, which leads also to mononuclear or binuclear complexes, is known[12]. However, the Cu(I) bpm system is not known so far. These complexes can be of potential interest since photocatalytic reduction of dicationic methyl viologen by similar copper(I) derivatives $[Cu(N\text{-}N)(PPh_3)_2]^+$ (N-N = 1.10-phenanthroline and 2,2'-bipyridine], have been recently reported[13].

Following our interest on coordination properties of P-donor ligand and its derivatives[14], we describe the synthesis and characterization of novel copper(I) complexes, which were obtained by reactions of the type:

$$[Cu(PR_3)_2(CH_3CN)_2]PF_6 + bpm \rightarrow [Cu(PR_3)_2(bpm)]PF_6 + 2CH_3CN$$

I ; R = Cy, bpm = 2,2'-bipyrimidine
II; R = Ph

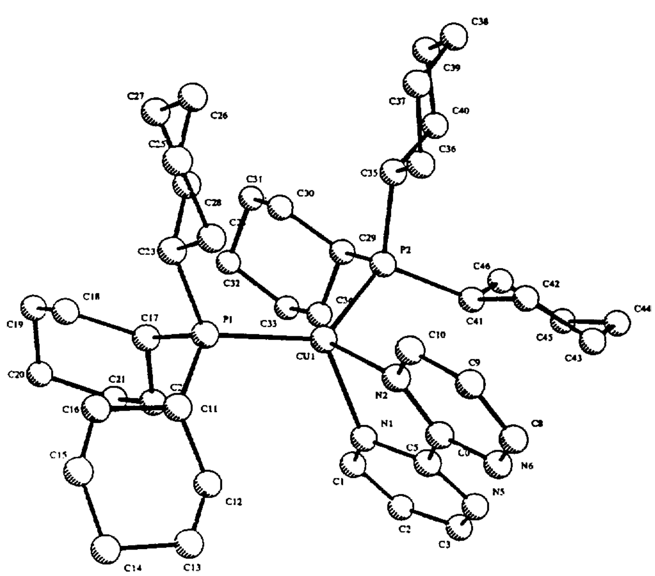


Figure 1. View of one of the two independent $[(Cy_3P)_2Cu(bpm)]PF_6$ complexes with the atom numbering scheme.

The reaction of $[Cu(PCy_3)_2(CH_3CN)_2]PF_6$ with bpm at room temperature gave a yellow solution. The Cu-bpm complex was isolated as air-stable orange crystal in 58% yield. The structure of compound I was deduced from its ^1H NMR, IR, and X-ray crystal structure analysis. The ^1H NMR spectrum of I in CD_2Cl_2 shows resonances which are characteristics for cyclohexyl protons along with three peaks at 8.34, 8.24, and 8.14 ppm, assigned to the three chemically non-equivalent hydrogens in the bpm ring. IR spectrum of I shows several characteristic vibrational bands for the bpm ligand. A single absorption in the 1560-1580 cm^{-1} region, due to C-N and C-C stretching, is observed for the bimetallic complexes and is characteristic for bpm complexes to bimetallic comples[15]. However, monometallic bpm complexes generally contain two bands in this region. Accordingly, two bands of I at 1565 and 1575 cm^{-1} indicate that the complex is monometallic bpm complex. Although these data support its formulation as complex with the copper metal coordinated to the bpm, the correct configuration on copper center is not certain. To get a geometrical information of the complex in the solid state, X-ray diffraction was carried out.

Description of the Structure. $[(Cy_2P)_2Cu(bpm)]PF_6$ (I). The overall structure consists of two independent four co-ordinate copper(I) cations whose structures are almost identical except for the cyclohexyl ring conformation and two well seperated hexachlorophosphate anions. The structure of one of the two independent cation and atom labelling of I are shown in Figure 1. Selected bond distances and angles are listed in Table 1. The copper atom is in a tetrahedral arrangement with a $[CuN_2P_2]$ chromophore. The copper atom is co-ordinated to two nitrogen atoms in bpm and to two phosphorus atoms in tricyclohexyl phosphines. The Cu-N distances [2.13 (1)-2.20 (2) Å] are longer than those of

Table 1. Selected bond lengths and angles in $[(Cy_3P)_2Cu(bpm)]PF_6$

Distances (Å)			
Cu(1)-P(1)	2.284(7)	N(1)-C(1)	1.33(2)
Cu(1)-P(2)	2.32(1)	N(1)-C(5)	1.42(3)
Cu(1)-N(1)	2.19(2)	N(2)-C(6)	1.36(2)
Cu(1)-N(2)	2.13(2)	N(2)-C(10)	1.38(2)
Cu(2)-P(3)	2.29(1)	P(3)-C(57)	1.91(2)
Cu(2)-P(4)	2.311(8)	P(3)-C(63)	1.90(2)
Cu(2)-N(3)	2.15(1)	P(3)-C(69)	1.89(2)
Cu(2)-N(4)	2.20(2)	P(4)-C(75)	1.86(2)
P(1)-C(11)	1.84(2)	P(4)-C(81)	1.86(2)
P(1)-C(17)	1.83(2)	P(4)-C(87)	1.85(2)
P(1)-C(23)	1.85(2)	P(6)-F(7)	1.54(2)
P(2)-C(29)	1.84(2)	P(6)-F(8)	1.58(3)
P(2)-C(35)	1.89(2)	P(6)-F(9)	1.59(2)
P(2)-C(41)	1.89(2)	P(6)-F(10)	1.62(2)
P(5)-F(1)	1.58(2)	P(6)-F(11)	1.54(2)
P(5)-F(2)	1.61(2)	P(6)-F(12)	1.62(2)
P(5)-F(3)	1.57(2)	N(3)-C(47)	1.37(2)
P(5)-F(4)	1.64(2)	N(3)-C(51)	1.31(2)
P(5)-F(5)	1.50(3)	N(4)-C(52)	1.29(2)
P(5)-F(6)	1.59(3)	N(4)-C(56)	1.32(2)
Angles (deg)			
P(1)-Cu(1)-P(2)	128.9(2)	Cu(1)-P(2)-C(35)	114.3(7)
P(1)-Cu(1)-N(1)	117.6(5)	Cu(1)-P(2)-C(41)	111.0(6)
P(1)-Cu(1)-N(2)	111.4(5)	Cu(2)-P(3)-C(57)	112.8(7)
P(2)-Cu(1)-N(1)	99.6(5)	Cu(2)-P(3)-C(63)	117.6(6)
P(2)-Cu(1)-N(2)	109.6(4)	Cu(2)-P(3)-C(69)	111.5(6)
N(1)-Cu(1)-N(2)	77.9(9)	Cu(2)-P(4)-C(75)	116.7(7)
P(3)-Cu(2)-P(4)	131.1(3)	Cu(2)-P(4)-C(81)	115.6(6)
P(3)-Cu(2)-N(3)	101.6(5)	Cu(2)-P(4)-C(87)	114.3(6)
P(3)-Cu(2)-P(4)	108.1(4)	Cu(1)-N(1)-C(1)	131(2)
P(4)-Cu(2)-P(3)	115.5(4)	Cu(1)-N(1)-C(5)	110(1)
P(4)-Cu(2)-P(4)	110.9(5)	Cu(1)-N(2)-C(6)	113(1)
N(3)-Cu(2)-N(4)	75.9(8)	Cu(1)-N(2)-C(10)	129(1)
Cu(1)-P(1)-C(11)	113.5(6)	Cu(2)-N(3)-C(47)	125(1)
Cu(1)-P(1)-C(17)	111.4(7)	Cu(2)-N(3)-C(51)	116(1)
Cu(1)-P(1)-C(23)	116.4(6)	Cu(2)-N(4)-C(52)	112(1)
Cu(1)-P(2)-C(29)	115.2(6)	Cu(2)-N(4)-C(56)	129(1)

Estimated standard deviations in the least significant figure are given parentheses.

other transition metal-bpm complexes: $[Cu_2(bpm)_2(H_2O)_4(OH)_2][ClO_4]_2\cdot 2H_2O$(*av.* 2.021 Å)[16], $[Fe(mac)bpm](ClO_4)_2\cdot 2H_2O$(*av.* 1,985 Å)[17], and $[Pt(mnt)(bpm)]\cdot$dmf(*av.* 2.051 Å)[18]. The Cu-N distances of complex I are quite close to those of other transition metal-bpm complexes: $[(hfa)_2Co(bpm)Co(hfa)_2]$(*av.* 2.155 Å)[19], and $[Re(bpm)(CO)_4](CF_3SO_3)$(*av.* 2.16 Å)[9]. The longer Cu-N distances in the present complex seem to arise from the trans influence of the phosphorus atoms of the phosphine ligands which acts as a π-electron acceptor. The bond angle about the copper atom, N-Cu-N, is 77.8°, which is similar to that of the complexes: $[Pt(mnt)(bpm)]\cdot$dmf(79.7°), $[Cu_2(bpm)_2(H_2O)_4(OH)_2][ClO_4]_2\cdot 2H_2O$(80.3°), $[(hfa)_2Co(bpm)Co(hfa)_2]$ (76.8°), and $[Fe(mac)bpm](ClO_4)_2\cdot 2H_2O$(77.4°). The Cu-P bond lengths of 2.284 and 2.32 Å are similar to those observed for $[Cu(PMe_3)_4]^+[CuCl_2]^-$ (2.270 Å)[20], $[Cu(PMe_3)_4]^+[CuMe_2]^-$ (2.269 and 2.253 Å)[21], and $[(PPh_3)_2CuO_2NO]$(2.256 Å)[22]. Figure 2 shows the relative orientation of the two independent cations which interact each other through π-π stacking of the bpm ligands.

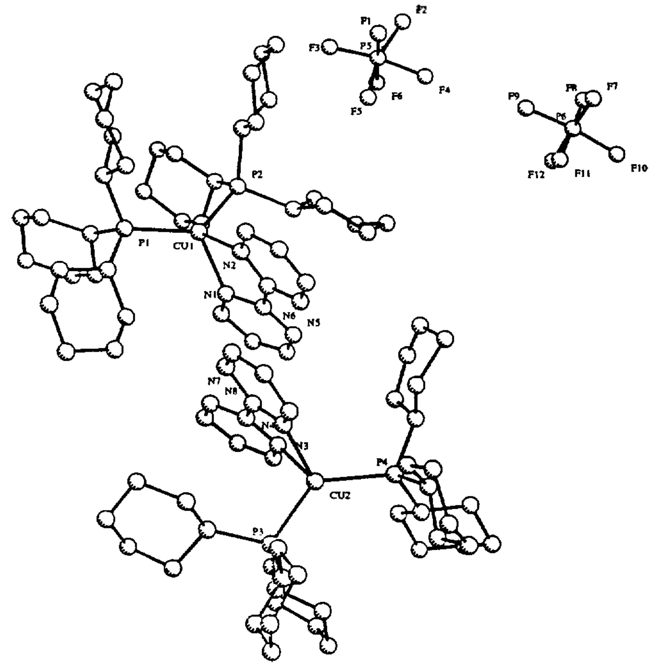


Figure 2. Relative orientation of the two indepedent $[(Cy_3P)_2Cu(bpm)]PF_6$ complexes.

Experimental Section

All manipulations of air-sensitive materials under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glove box. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer in CD_2Cl_2. Chemical shifts were referenced relative to an internal standard Me_4Si. IR spectra were measured on a Perkin-Elmer 1310 spectrometer. Elemental analyses were carried out at the Department of Chemistry, Liverpool University. Reagent grade CH_2Cl_2 and CH_3CN were distilled under argon from P_2O_5. The compounds $[Cu(CH_3CN)_4](PF_6)$[23] and $[Cu(CH_3CN)_2(PPh_3)_2]PF_6$[10] were prepared according to literature methods. Bipyrimidine (bpm) was purchased from Lancaster.

Preparation of $[(Cy_3P)_2Cu(bpm)]PF_6$ (Cy=cyclohexyl) (I). A mixture of $Cu(CH_3CN)_4PF_6$ (0.5 g, 1.34 mmol) and tricyclohexylphosphine (0.776 g, 2.77 mmol) in CH_2Cl_2 (25 m*l*) was stirred for 12h at room temperature. To this solution was added bpm (0.11 g, 0.69 mmol) in CH_2Cl_2 (10 m*l*) dropwise. The volume was reduced to *ca.* 15 m*l* and yellow product was collected by addition of hexane (15 m*l*). Recrystallization from saturated methylene dichloride sealed with septum produced yellow single crystals suitable to X-ray structure determination. The yield was 57%. mp. 194℃. ^1H NMR (CD_2Cl_2) δ8.34 (s, 2H), 8.24 (s, 2H), 8.14 (s, 2H), 2.72~1.88 (m, 33H, Cy); IR (on KBr pellet; cm^{-1}) ν (CC or CN) 1575, 1565. Anal. Calcd. for $C_{44}H_{72}CuN_4F_6P_3$: C, 56.93; H, 7.76. Found: C, 56.21; H, 7.48.

Preparation of $[(Ph_3P)_2Cu(bpm)]PF_6$(II). To a stirred CH_2Cl_2 solution (20 m*l*) of $[Cu(CH_3CN)_2(PPh_3)_2]PF_6$ (0.3 g, 0.36 mmol) was added bpm (0.029 g, 0.18 mmol) in CH_2Cl_2 (20 m*l*) dropwise. The solution was stirred at room temperature for 4h. During which time the solution was turned into deep orange. The orange solution was filtered and the volume was reduced to *ca.* 10 m*l*. Orange solid obtained upon addition of hexane (20 m*l*) were dried under vacuum. Recrystallization from methylene dichloride produced amorphous solid and yellow crystals suitable to an X-ray determination. The yield was 63%, mp. 202℃. ^{1}H NMR (CD_2Cl_2) δ 8.32 (s, 2H), 8.20 (s, 2H), 8.10 (s, 2H); IR (on KBr pellet; cm^{-1}) ν (CC or CN) 1573, 1565. Anal. Calcd. for $C_{44}H_{36}CuN_4F_6P_3$; C, 59.23; H, 4.04. Found: C, 58.89; H, 3.92.

X-ray data collection and structure refinement. A yellow prism crystal of I having approximate dimensions of 0.45×0.45×0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated MoK_α radiation and a 12 KW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range of $26.78<2\theta<32.98°$ corresponds to a monoclinic cell with dimensions: $a=23.7$ (1) Å, $b=11.7$ (1) Å, $c=34.39$ (6) Å, $V=9454$ Å^3, $\beta=99.6$ (2)°, $Z=8$ and $d_{calc}=1.296$ g/cm^3. Based on the systematic absence *hkl*: $h+k\neq 2n$; *hOl*: $l\neq 2n$, packing considerations, a statistical analysis of intensity distribution, the space group was determined to be *Cc*. The data were collected at a temperature of 25± 1℃ using the ω scan technique to a maximum 2θ value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a take-off angle of 6.0°. The weak reflection ($I<4.0\ \sigma(I)$) were rescanned and the counts were accumulated to assume good counting statistics.

The structure was solved by direct methods. The final least-squares refinement included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the copper, phosphorus, and some of the nitrogen atoms and carbon atoms of the bpm ligand, isotropic thermal parameters for the rest of non-hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on 5359 observed reflections ($I>4.00\ \sigma(I)$) and 571 variable parameters and converged with unweighted and weighted agreement factors of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.090$ and $R_W=[\Sigma_W(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}=0.099$. The standard deviation of unit weight was 3.30. The weighting scheme was based on counting statistics and included a factor ($p=0.03$) to downweight the intense reflections. Neutral atom scattering factors were taken from Cromer and Waber[24]. Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer[25]. All calculations were performed using the TEXSAN.[26] crystallographic software package of Molecular Structure Cororation.

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Supplementary Material Available. Tables of fractional coordinates and isotropic temperature factors for the hydrogen atoms, additional bond lengths and angles, and anisotropic temperature factors for *I* (31 pages). Supplementary materials are available from one of the authors (J. Ko) upon request.

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