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Preparation, Electronic Properties and Crystal Structure of Imidazolebis(1,10-phenanthroline)copper(II) Bis(hexafluorophosphate)

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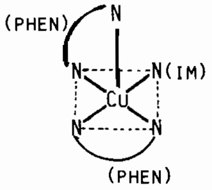
Abstract

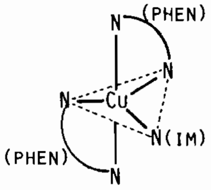
A copper(II) complex with imidazole (im) and 1,10-phenanthroline (phen), $[Cu(phen)_2(im)](PF_6)_2$ has been prepared. The crystal structure has been determined by the X-ray diffraction method: monoclinic, space group $P2/c$, $a = 16.866(5)$, $b = 14.919(3)$, $c = 12.417(3)$ Å, $\beta = 105.86(2)°$, $D_m = 1.72$, $D_c = 1.73$ g cm^{-3}, $Z = 4$, $R = 0.068$ and $R_w = 0.075$ for 3262 observed reflections. The geometry around the copper atom is an elongated octahedron. The basal plane is formed by an imidazole nitrogen atom, two nitrogen atoms of phen and one nitrogen atom of the second phen. The other nitrogen atom of the second phen and the fluorine atom of PF_6^- occupy the apical positions. The electronic and ESR spectra are compatible with the crystal structure.

Introduction

Copper(II) complexes with imidazole ligand have been extensively studied as simple model compounds for metal–imidazole interactions in biological systems. So far, many complexes with various ratios of imidazole to copper have been prepared and characterized [1]. In view of the importance of copper–imidazole complexes, we have initiated the preparation of copper complexes with mixed ligands containing imidazole. In this study, we have isolated $[Cu(phen)_2(im)](PF_6)_2$ (**1**) (phen = 1,10-phenanthroline, im = imidazole) as blue crystals. Although some copper complexes containing only one imidazole have been structurally characterized [2, 3], it is interesting to see the structure of this complex, since a five-coordinate tetragonal pyramidal (**A**) or trigonal bipyramidal (**B**) structure can be assigned to the geometry around the copper atom based on the steric effect in bis-chelated metal complexes of 1,10-phenanthroline [4]. Thus we have determined the X-ray crystal structure of **1** and examined its electronic properties in order to clarify the coordination environment of the copper atom.



A



B

Experimental

Preparation of the Complex

Copper(II) acetate monohydrate (50 mg) and phen (99 mg) were dissolved in methanol and warmed at 60 °C. To this was added a methanol solution of NH_4PF_6 with stirring to give a blue precipitation. A solution of imidazole (14 mg) in water was added to this mixture with stirring and warming. The resulting blue solution was filtered and left to stand overnight to give blue crystals. The crystals were collected and desiccated over P_2O_5. *Anal.* Found: C, 41.19; H, 2.60; N, 10.95. Calc. for $C_{27}H_{20}CuF_{12}N_6P_2$: C, 41.47; H, 2.58; N, 10.75%.

Measurements

Electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer at room temperature. ESR spectra were measured on a Jeol JES-FE2XG ESR spectrometer (X-band microwave unit, 100 KHz field modulation) equipped with an Air Product LTD-3-110 liquid helium transfer system. The microwave frequency was monitored with a Takeda Riken TR5212 microwave counter, and the resonance

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magnetic field values of the signals were measured with an NMR field meter (ECHO Electronics Co., Ltd.).

TABLE 1. Atomic Coordinates ($\times 10^4$)

Atom	x	y	z
Cu	2432(1)	2737(1)	7314(1)
PA	0	2835(2)	7500
PB	5000	4047(3)	2500
PC	5000	−143(2)	2500
PD	0	1465(3)	2500
FA1	0	1792(6)	7500
FA2	0	3848(6)	7500
FA3	964(3)	2798(5)	7891(5)
FA4	−9(4)	2846(5)	8744(5)
FB1	4842(6)	4045(7)	1232(5)
FB2	4349(6)	3368(7)	2452(8)
FB3	5681(6)	4727(6)	2635(9)
FC1	5000	−1203(4)	2500
FC2	5000	921(4)	2500
FC3	4989(3)	−135(3)	1217(3)
FC4	4022(2)	−137(3)	2155(4)
FD1	369(13)	512(7)	2637(24)
FD2	405(10)	2370(9)	2413(14)
FD3	−84(6)	1445(5)	1211(6)
FD4	888(7)	1483(11)	2773(10)
N1	1723(3)	3497(4)	6046(5)
N2	2651(3)	3937(4)	8069(4)
N3	2110(4)	1579(4)	6440(5)
N4	3417(4)	2640(4)	6445(5)
N5	2870(4)	2075(4)	8737(5)
N6	3723(5)	1312(5)	10039(6)
C1	1248(5)	3237(6)	5046(6)
C2	807(5)	3870(6)	4276(7)
C3	855(5)	4771(6)	4525(7)
C4	1342(5)	5063(5)	5594(7)
C5	1767(4)	4385(5)	6330(6)
C6	2261(4)	4625(5)	7415(6)
C7	2332(5)	5519(5)	7757(7)
C8	2821(5)	5710(6)	8848(8)
C9	3217(5)	5019(6)	9497(7)
C10	3128(5)	4125(6)	9102(6)
C11	1414(6)	5983(6)	5968(8)
C12	1887(6)	6212(6)	7004(8)
C13	1499(5)	1039(5)	6514(8)
C14	1250(7)	294(6)	5777(8)
C15	1630(6)	150(7)	4958(9)
C16	2280(6)	695(6)	4893(7)
C17	2514(5)	1405(5)	5666(6)
C18	3188(5)	1967(6)	5648(6)
C19	3632(6)	1833(7)	4829(7)
C20	4294(7)	2414(7)	4855(8)
C21	4517(6)	3087(7)	5661(8)
C22	4052(5)	3190(6)	6479(7)
C23	2695(7)	588(7)	4064(8)
C24	3354(7)	1124(7)	4025(7)
C25	3567(5)	1611(5)	8965(7)
C26	3109(6)	1588(6)	10488(7)
C27	2566(6)	2062(6)	9657(7)

X-ray Crystal Structure Analysis

The crystal used was ground to a sphere (radius 0.14 mm). The unit cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 20 ± 1 °C.

Crystal data: $C_{27}H_{20}CuF_{12}N_6P_2$, M = 781.97; monoclinic; $P2/c$; a = 16.866(5), b = 14.919(3), c = 12.417(3) Å; β = 105.86(2)°; D_m = 1.72; D_c = 1.73 g cm^{-3}; Z = 4; μ(Mo Kα) = 9.4 cm^{-1}.

The intensity data were collected by the $2\theta-\omega$ scan technique with a scan rate of 4° min^{-1}. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. A total of 4365 reflections with $2\theta < 50°$ were collected. The intensity data were corrected for Lorentz-polarization effects and for absorption. Independent 3262 reflections with $|F_o| > 3\sigma(F_o)$ were considered as 'observed' and were used for the structure analysis.

The structure was solved by the heavy atom method. Refinement was carried out by the block-diagonal least-squares method. The weighting scheme $w = [\sigma_{\mathrm{count}}^2 + (0.015|F_o|)^2]^{-1}$ was employed. Hydrogen atoms were not included in the calculation. The final discrepancy factors were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.068$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.075$.

All the calculations were carried out on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science by the use of the UNICS-III programs [5]. The final atomic coordinates are given in Table 1 and the main bond lengths and bond angles in Table 2.

Results and Discussion

The crystal structure consists of $[Cu(phen)_2(im)]^{2+}$ cations and PF_6^- anions. Of the four crystallographically independent PF_6^- ions (all the P atoms of these PF_6^- ions occupy two-fold special positions), one (designated as PA, FA1, FA2, FA3, FA3′, FA4 and FA4′) is weakly coordinated to the copper atom (Cu---FA3 2.762(6) Å) and the others do not participate in any coordination. A perspective drawing

TABLE 2. Selected Bond Lengths (Å) and Angles (°)

Cu–N1	2.042(5)	Cu–N4	2.219(7)
Cu–N2	2.008(6)	Cu–N5	1.982(5)
Cu–N3	2.034(6)	Cu–FA3	2.762(6)
N1–Cu–N2	81.9(2)	N2–Cu–N4	102.6(2)
N1–Cu–N3	92.6(3)	N2–Cu–N5	93.0(2)
N1–Cu–N4	91.1(2)	N3–Cu–N4	79.1(3)
N1–Cu–N5	164.1(3)	N3–Cu–N5	91.9(2)
N2–Cu–N3	174.2(2)	N4–Cu–N5	104.8(2)

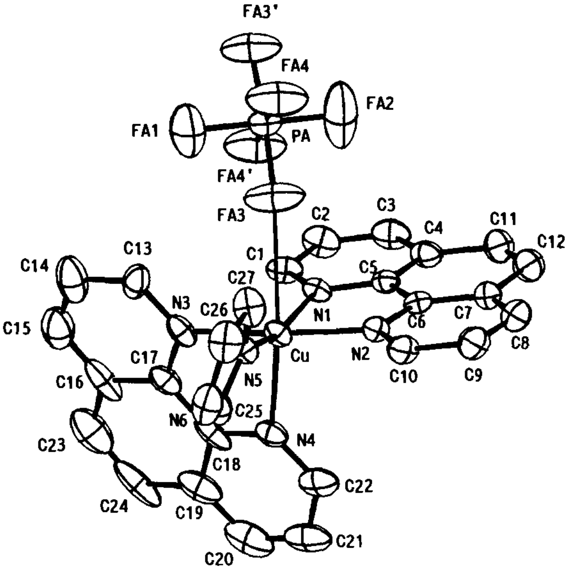

Fig. 1. ORTEP diagram of $[Cu(phen)_2(im)(PF_6)]^+$.

of the complex cation is illustrated in Fig. 1. The copper atom is coordinated by two nitrogen atoms of phen, N1 and N2, a nitrogen atom of the second phen, N3, and an imidazole nitrogen atom, N5, at distances 2.042(5), 2.008(6), 2.034(6) and 1.982(5) Å, respectively. The copper atom is further coordinated by the other nitrogen atom of the second phen, N4, and the fluorine atom of the hexafluorophosphate ion, FA3, at the distances of 2.219(7) and 2.762(6) Å, respectively. Thus, the coordination geometry may be described as an elongated octahedron. The *cis*-octahedral configuration appears in the complexes, $[Cu(phen)_2X]Y$ [6] and $[Cu(phen)_2Z_2]$ [7] (where X = CH_3COO^-, $HCOO^-$, NO_2^-; Y = ClO_4^-, BF_4^-, NO_3^-; Z = NCS^-, $NCSe^-$). This configuration is close to a tetragonal pyramid (A) if we neglect the semicoordination of PF_6^-. One of the interesting features of this structure is that the imidazole ring is inclined by 68.4° to the equatorial plane. A similar orientation is observed in $[Cu(tmen)(im)_2](ClO_4)_2$ (tmen = *N,N,N',N'*-tetramethylethylenediamine) [8].

The electronic reflectance spectrum of **1** shows two bands at 11.4 × 10^3 and 16.0 × 10^3 cm^{-1}. In acetonitrile, the complex shows an absorption band at 14.9 × 10^3 cm^{-1} (ϵ = 86 dm^3 mol^{-1} cm^{-1}) with a shoulder at 11.5 × 10^3 cm^{-1}. Similar electronic spectra are observed for the *cis*-distorted-octahedral CuN_4O_2 chromophores of the $[Cu(phen)_2X]Y$ complexes [6] and CuN_4N_2 chromophores of the $[Cu(phen)_2Z_2]$ complexes [7].

X-band ESR spectrum of the acetonitrile solution of **1** shows a broad band isotropic signal at g = 2.08 at room temperature. At 12 K, the spectrum becomes clearly axial with $g_{\parallel}$ = 2.25 ($A_{\parallel}$ = 173 G) and $g_{\perp}$ = 2.05 suggesting a $d_{x^2-y^2}$ ground state consistent with the elongated octahedral stereochemisty of the complex.

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