

Crystal Structure of Adduct 2-Phenyl-imidazo[4,5-f]1,10-phenanthroline Methanol

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The structure of the title adduct comprises a phenanthroline derivative 2-phenyl-imidazo[4,5-f]1,10-phenanthroline and a methanol. The composition of the crystalline adduct was characterized as C₁₉H₁₂N₄·CH₃OH. It belongs to orthorhombic system, space group *Pna*2₁ with *a* = 1.3693(4) nm, *b* = 2.2988(7) nm, *c* = 0.51338(15) nm, *V* = 1.6160(8) nm³, *Z* = 4, and final *R*₁ = 0.0423, *wR*₂ = 0.1012. Crystal structure shows that all the 19 carbon atoms and 4 nitrogen atoms are coplanar. The bond length data indicated that a very extensive conjugation system was formed. This conjugation makes the compound being a potentially excellent energy transformer used for luminescent materials.

Keywords 1,10-phenanthroline derivative, crystalline adduct, crystal structure, 2-phenyl-imidazo[4,5-f]1,10-phenanthroline

Introduction

1,10-Phenanthroline and its derivatives are excellent neutral ligands duo to their extensive conjugation property and therefore are widely used to synthesize the luminescence and laser materials.^{1,2} The introduction of the neutral ligands to the europium β-diketonato complexes could improve the volatility, thermal stability and carrier-transport ability of the europium complexes, and thus greatly enhances the photoluminescent and electroluminescent properties.^{3,4} The neutral ligands that can form these ternary complexes with the tris-β-diketonates include heterocyclic nitrogen donors such as pyridine, 2,2'-dipyridyl and 1,10-phenanthroline as well as oxygen donors such as triphenylphosphine oxide, pyridine-*N*-oxide and 1,10-phenanthroline-*N*-oxide.⁵⁻⁷ A lot of experiments indicate that the conjugation property of a neutral ligand is important for the luminescent efficiency of luminescent materials. To the best of our knowledge, the crystal structure of the title compound has not been reported yet. In this paper, the crystal structure which is a big conjugation system is reported and their chemical and physical properties are discussed. Crystal structure shows that all the 19 C atoms and 4 N atoms are coplanar. The bond length data indicated that a very extensive conjugation system was formed.

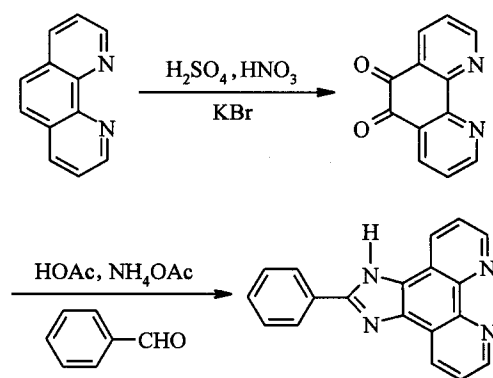
This conjugation makes the compound being a potentially excellent energy transformer used for a luminescent material.

Experimental

General procedure

All starting materials were of analytical grade. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. UV spectra in methanol solution were measured on an WFZ-900-D4 spectrophotometer. IR spectra (KBr pellet) were recorded on a Nicolet FT-IR 170SX spectrometer in the 400—4000 cm⁻¹ region. The ¹H NMR spectra in deuterium chloroform were recorded on a Varian Inova-500 NMR spectrometer. The m.p. was measured with a RY-1A melting point apparatus. The reaction is shown in Scheme 1.

Scheme 1



Preparation of 1,10-phenanthroline-5,6-dione

This compound was prepared according to the reported method.⁸ The product is yellow powder, yield 70%, m.p. 256—258 °C; ¹H NMR (DCCl₃, 500 MHz) δ: 9.14 (q, *J* = 5, 2 Hz, 2H, N = CH), 8.53 (q, *J* = 8, 5 Hz, 2H, O = C - C = CH), 7.60 (q, *J* = 8, 2 Hz, 2H,

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N = C - CH); IR (KBr) ν : 1685 (vs), 1414 (vs); 1577 (s), 1560 (s), 1459 (s), 1293 cm^{-1} (s), 1316 (m), 1205 (m), 740 (m), 1703 (w), 1115 (w), 1010 (w), 925 (w), 817 (w), 808 (w) cm^{-1} .

Preparation of the adduct 2-phenyl-imidazo[4,5-f]1,10-phenanthroline methanol

According to the reported method,^{9,10} 1,10-phenanthroline-5,6-dione (5 mmol) and ammonium acetate (100 mmol) were dissolved in 30 mL of glacial acetic acid. Then 2 mL of benzaldehyde was added into the reacting solution. After keeping reaction at 85–90 °C for 3 h, the reacting mixture was neutralized with an ammonia solution to pH = 8–9, and then a yellow solid product was obtained and recrystallized from a solvent mixture of methanol and tetrahydrofuran. The filtrate stood at room temperature for two weeks and then the yellow crystals suitable for X-ray crystal analysis were obtained. The crystals were characterized to have a formula of $\text{C}_{19}\text{H}_{12}\text{N}_4 \cdot \text{CH}_3\text{OH}$. It was dried in an oven at 50–60 °C. Yield 70%, m.p. 300 °C; ^1H NMR (DCCl_3 , 500 MHz) δ : 10.60 [d, J = 8.5 Hz, 2H, N = C - H, (phenanthroline)], 9.06 [q, J = 5 Hz, 2H, N = C - C = CH (phenanthroline)], 8.98 [t, J = 8 Hz, 2H, N - C - C = CH (phenyl)], 8.09 [q, J = 8.5, 5 Hz, 2H, N = C - CH = (phenanthroline)], 7.53 [d, J = 8 Hz, 3H, (phenyl)]. Anal. calcd for $\text{C}_{19}\text{H}_{12}\text{N}_4$: C 77.02, H 4.05, N 18.92; found C 77.01,

H 3.74, N 18.25. Analysis shows that the dried product is demethanolic compound.

X-Ray structure of the adduct

Single crystal X-ray diffraction measurement of $\text{C}_{19}\text{H}_{12}\text{N}_4 \cdot \text{CH}_3\text{OH}$ was carried out with a Brüker SMART 1000 CCD diffractometer equipped with a graphite monochromator the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo $K\alpha$ radiation (λ = 0.071073 nm) at (298 ± 2) K. The unit cell dimensions were obtained with least square refinements. The structure was solved by direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 program.¹¹ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on the calculated positions and assigned with isotropic displacement parameters.

A total of 6399 reflections were measured in the range $2.31^\circ < \theta < 25.03^\circ$. The 2581 reflections were independent, applying the criterion $I > 2\sigma(I)$. The crystal system is orthorhombic, space group $Pna2_1$ with cell dimensions of a = 1.3693(4) nm, b = 2.2988(7) nm, c = 0.51338(15) nm, V = 1.6160(8) nm^3 , Z = 4, R_1 = 0.0423, wR_2 = 0.1012.

The details of crystal data and structure refinement are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1 Crystal data and structure refinement of the title compound

Molecular formula	$\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}$
Formula weight	328.37
Temperature (K)	298 ± 2
Color and habit	Yellow prism
Crystal size (mm^3)	0.30 × 0.25 × 0.20
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell parameters	
a (nm)	1.3693(4)
b (nm)	2.2988(7)
c (nm)	0.51338(15)
V (nm^3)	1.6160(8)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Z	4
$F(000)$	688
D_c (g/cm^3)	1.350
Radiation	Graphite-monochromatized Mo $K\alpha$
λ (nm)	0.071073
Absorption correction	Multi-scan
Scan type	φ and ω scans
θ_{max} (°)	25.03

Continued

Data collection range	$-16 \leq h \leq 12,$ $-27 \leq k \leq 27,$ $-6 \leq l \leq 5$
Reflections measured	Total: 6399 unique: 2581 [$R(\text{int}) = 0.0329$]
Refinement method	full-matrix least-squares on F^2
Absorption coefficient (μ) (mm^{-1})	0.087
Min. transmission	0.9744
Max. transmission	0.9828
Final R indices	
R_1	0.0423
wR_2	0.1012
R indices (all data)	
R_1	0.0626
wR_2	0.1085
Goodness of fit on F^2	1.070

Table 2 Selected bond lengths and bond angles

Bond lengths (nm)			
N(1)—C(7)	0.1365(3)	C(14)—N(3)	0.1360(3)
N(1)—C(19)	0.1371(3)	C(9)—C(10)	0.1404(4)
N(2)—C(7)	0.1328(3)	C(10)—C(11)	0.1369(4)
N(2)—C(8)	0.1387(3)	C(11)—C(12)	0.1396(4)
C(1)—C(2)	0.1382(4)	C(12)—N(4)	0.1319(3)
C(1)—C(6)	0.1386(4)	C(13)—N(4)	0.1352(4)
C(2)—C(3)	0.1371(4)	C(13)—C(14)	0.1460(4)
C(3)—C(4)	0.1360(5)	C(14)—C(18)	0.1414(4)
C(4)—C(5)	0.1377(4)	C(15)—N(3)	0.1327(4)
C(5)—C(6)	0.1381(4)	C(15)—C(16)	0.1388(5)
C(6)—C(7)	0.1467(4)	C(16)—C(17)	0.1371(4)
C(8)—C(19)	0.1380(3)	C(17)—C(18)	0.1413(4)
C(8)—C(9)	0.1425(4)	C(18)—C(19)	0.1424(3)
C(9)—C(13)	0.1414(3)	N(1)—O(1)	0.2816
		N(3A)—O(1)	0.2945
Bond angles ($^\circ$)			
C(7)—N(1)—C(19)	106.8(2)	C(7)—N(2)—C(8)	104.45(19)
C(2)—C(1)—C(6)	120.8(3)	C(3)—C(2)—C(1)	120.0(3)
C(4)—C(3)—C(2)	119.3(3)	C(3)—C(4)—C(5)	121.5(3)
C(6)—C(5)—C(4)	120.0(3)	C(5)—C(6)—C(1)	118.4(2)
C(5)—C(6)—C(7)	119.6(2)	C(1)—C(6)—C(7)	122.0(2)
N(2)—C(7)—N(1)	112.4(2)	N(1)—C(7)—C(6)	123.1(2)
C(19)—C(8)—N(2)	110.3(2)	C(19)—C(8)—C(9)	121.0(2)
C(13)—C(9)—C(10)	117.6(2)	C(13)—C(9)—C(8)	118.2(2)
C(11)—C(10)—C(9)	119.6(3)	C(10)—C(11)—C(12)	118.1(3)
N(4)—C(12)—C(11)	124.7(3)	N(4)—C(13)—C(9)	122.6(2)
C(9)—C(13)—C(14)	119.9(2)	N(3)—C(14)—C(18)	121.5(2)
C(18)—C(14)—C(13)	121.1(2)	C(15)—N(3)—C(14)	117.4(3)
C(12)—N(4)—C(13)	117.3(2)	N(3)—C(15)—C(16)	125.2(3)
C(17)—C(16)—C(15)	118.5(3)	C(16)—C(17)—C(18)	118.6(3)
C(14)—C(18)—C(17)	118.8(2)	C(14)—C(18)—C(19)	116.6(2)
C(8)—C(19)—C(18)	123.2(2)	C(8)—C(19)—N(1)	106.0(2)

Results and discussion

As shown in Fig. 1, all the 19 carbon atoms and 4 nitrogen atoms of the title compound were used to calculate the least-squares plane with the XP program. The distances of the C and N atoms from this least-squares plane showed that the smallest deviation is -0.01233 nm for C(1) and the largest is 0.01424 nm for C(4), and the mean deviation is 0.00708 nm. This indicated that all these atoms are very close to the least square plane, suggesting that all the C and N atoms were linked together with an sp^2 hybridization.

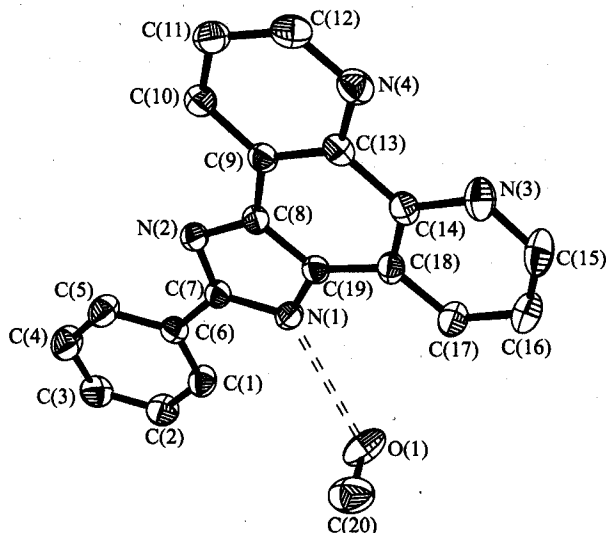


Fig. 1 Structure of $C_{19}H_{12}N_4 \cdot CH_3OH$, H atoms are omitted for clarity.

The longest bond length, 0.1467 nm is that of the C(6)—C(7) bond linking the benzene and imidazole and is expectedly shorter than that of normal single C—C bond (0.154 nm), and the shortest bond length is that of C(7)—N(2), 0.1328 nm. The average bond length, 0.138 nm, of all the 19 C atoms and 4 N atoms suggested that all π -electrons of the C and N atoms are delocalized over the whole molecule. This structure would be ideal for transporting energy in its luminescent complexes.

N(3) and N(4) may form a chelate ring with a metal ion, while N(1) and N(2) can not, that explains why the coordinating ability of N(3) and N(4) is stronger than that of N(1) and N(2).

In crystal, 2-phenyl-imidazo[4,5-*f*]1,10-phenanthroline molecules were linked each other by methanol molecules. There are two kinds of hydrogen bond, N(1)—H(1C)···O(1) (0.2816 nm) and O(1)—H(1B)···N(3A) [N(3A) from another molecule 0.2945 nm]. With these hydrogen bonds, methanol bridged 2-phenyl-imidazo-[4,5-*f*]1,10-phenanthroline molecules to form a two-dimensional network (Fig. 2).

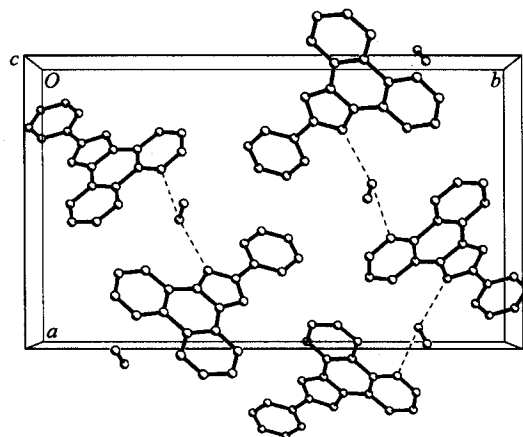


Fig. 2 Packing arrangement in a unit cell of the adduct.

The H atom attached to N(1) may be replaced by other atoms or substituents¹ and therefore its hydrophilic nature would be modified by the substitution, and then the properties of EL materials containing this ligand would be improved.

Another feature of this structure is that the imidazole ring which appears as if an aromatic amine compound would present an excellent ability of carrier-transport electronic hole.⁴ Therefore, it could be used in developing new luminescent materials.

In the weak acidic solution, N(3) or N(4) easily combines with H^+ , for example, an adduct was gained with a composition of $2(C_{19}H_{12}N_4) \cdot 4HCl \cdot 3H_2O$ by adding a little of dilute hydrochloric acid into the ethanol solution of the $C_{19}H_{12}N_4$. Of course, the $C_{19}H_{12}N_4$ and its salts are more easily dissolved in stronger acid solution. For this reason, the preparation of its complexes should be carried out in a neutral or weak basic solution.

UV and IR spectra

The UV spectrum of the compound in methanol solution showed three absorption bands at 221, 281, 290 nm which can be attributed to the $\pi \rightarrow \pi^*$ transitions. These absorption bands showed a bathochromic shift compared to the spectrum of parent compound 1,10-phenanthroline (at 216, 240, 268.5 nm, respectively). This result indicated that an extensive conjugation system in the title compound led to a decrease in transition-energy of the π electrons.

The main IR (in KBr pellet) data and their assignments are summarized in Table 3. The assignments are made by the comparison with the related compounds, and the corresponding functional groups.¹² The ring vibrations were observed at 1476, 1458, 1448, 1427 cm^{-1} for the four rings of the molecule, respectively. The C—H out-of-plane bending vibrations appeared at 769, 701, 685 cm^{-1} . These are evidently different from those of the parent 1,10-phenanthroline molecule.

Table 3 IR data (cm^{-1}) of the title compound and 1,10-phenanthroline^a

Assignments	$\nu(\text{N—H})$	$\nu(\text{C—H})$	$\nu(\text{C=N})$	$\nu_{\text{as}}(\text{C=C})$	$\nu(\text{C=C})$	$\delta(\text{C—H})$	$\pi(\text{C—H})$
						1476 (m)	
Title compound	3430 (w)	3115 (m) 3067 (m)	1617 (w) 1601 (w)	1562 (s) 1546 (w)	1458 (vs) 1448 (m)	1397 (s) 1351 (s) 1427 (w)	739 (vs) 701 (vs) 685 (s)
1,10-Phenanthroline	3382 (s)	3040 (m)	1643 (m)	1615 (m) 1586 (m)	1503 (s) 1497 (m)	1421 (vs)	853 (vs) 739 (vs)

^a Assignment: ν = stretching, δ = in-plane bending, π = out-of-plane bending, as = asymmetric.

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