Synthesis and Characterization of 2,6-Bis(imino)phenoxy Cobalt Complexes

HAN, Ling-Qin[a,b](韩玲芹) **SUN, Wen-Hua***[,a](孙文华) **WANG, Le-Yong**[a](王乐勇)
SHAO, Chang-Xing[a](邵长星) **WANG, Hong-Gen**[c](王宏根) **LI, Ji-Tai**[b](李记太)
[a] *State Key Laboratory of Engineering Plastics and The Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[b] *Department of Chemistry, Hebei University, Baoding, Hebei 071002, China*
[c] *State Key Laboratory of Functional Polymer, Nankai University, Tianjin 300071, China*

A series of cobalt complexes bearing 2,6-bis(imino)phenoxy ligands, $LCoCl_2$ [L = 2,6-$(ArNCH)_2CH_3C_6H_2OH$] was synthesized by the reaction of the ligand 2,6-bis(imino)phenol with the equivalent mole of cobalt dichloride, and these complexes were characterized by elemental analyses, ^1H NMR, MS and IR spectra. The structure of one complex was determined by single crystal X-ray diffraction analysis.

Keywords cobalt complex, Schiff-base, crystal structure

Introduction

Recent research efforts have been devoted to the study of late transition metal complexes as model systems for the polymerization or oligomerization of ethylene.[1-3] The most notable achievements have been done by Brookhart,[4] Bennett,[5] and Gibson groups.[6,7] They independently reported the cationic iron and cobalt catalytic systems with high activity for the polymerization of ethylene. Approximately, at the same time of developing the cationic iron and cobalt catalysts, a new class of neutral nickel catalysts based on salicylaldiminato with [N, O] chelating bidentate ligands was reported by Johnson[8] and Grubbs.[9-11] These compounds showed high activity for ethylene polymerization under mild conditions in the presence of a phosphine scavenger such as $Ni(COD)_2$ or $B(C_6F_5)_3$. It is promising to use Schiff-base phenolic coordinated late-transition metal complexes for olefin polymerization. Therefore it would be interesting to synthesize and explore the application of the Schiff-base phenolic ligand. Recently, we have investigated a series of 2,6-bis(imino)-phenoxy derivatives and their cobalt and nickel incorporated species, which show moderate activity in mild condition using the co-catalyst methylaluminoxane (MAO).[12] Here, we would like to report the synthesis, characterization and structure of cobalt complexes bearing bulky 2,6-bis(imino)phenoxy derivative ligands, as well as discussion of the interaction between molecules in the solid state of the complex (**6**).

Experimental

Instruments

All manipulations were carried out under nitrogen atmosphere using standard Schlenk and Cannula techniques. Elemental analyses were performed by an HP-MOD 1106 microanalyzer. ^1H NMR spectra were recorded on a Bruker spectrometer DMX-300 with TMS as the internal standard. IR spectra were obtained with KBr pellets on a Perkin-Elmer FT-IR 2000 spectrometer. Mass spectra were measured on a Kratos AEI MS-50 instrument using fast atom bombardment (FAB) or electron impact (EI) technology. Melting points were determined with a digital electrothermal apparatus without correction.

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* E-mail: whsun@infoc3.icas.ac.cn; Fax: 86-10-62559373

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Materials

2-Hydroxy-5-methylisophthaldehyde was prepared according to the reported procedure.[13] Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. The substituted anilines were purchased from Aldrich Chemical Co. All other chemicals were obtained commercially and used as received unless stated otherwise.

Syntheses of ligands and complexes

2,6-Diformyl-4-methylphenoxy-bis (*2,6-dimethylanil*) (**1**) To a solution of 2-hydroxy-5-methylisophthaldehyde (1.10 g, 6.70 mmol) and a few drops of glacial acetic acid in anhydrous ethanol (15 mL) under N_2 at 50 ℃, the 15 mL of ethanol solution of 2,6-dimethylaniline (2.44 g, 20.12 mmol) was added within 10 min. The mixture was heated under reflux for further 30 min. Upon cooling to room temperature, the solvent volume was reduced to about 15 mL under vacuum, and the residue was crystallized from ethanol at −20 ℃ to give the yellow powder 1.77 g in 71.4% yield. M.p. 136—137 ℃; ^{1}H NMR ($CDCl_3$) δ: 13.52 (s, 1H, ArOH), 8.32—8.60 (br, 2H, HC=N), 7.16—7.00 (m, 8H, ArH), 2.46 (s, 3H, $ArCH_3$), 2.25 (s, 12H, $ArCH_3$); IR (KBr) ν: 3446 (br, m, OH), 2919 (m), 1630 (vs, C=N), 1588 (vs, C=N), 1468 (vs), 1311 (m), 1194, 1091, 1036, 980, 768, 619, 556 cm^{-1}; EI-MS *m/z* (%) 370 (M^+, 5.4), 265 [$M^+ - C_6H_3(CH_3)_2$, 7.5], 251 [$M^+ - C_6H_3(CH_3)_2N$, 15.0], 250 [$M^+ - C_6H_3(CH_3)_2 - CH_3$, 83.2]. Anal. calcd for $C_{25}H_{26}N_2O$: C 81.08, H 7.03, N 7.56; found C 80.79, H 6.98, N 7.48.

2,6-Diformyl-4-methylphenoxy-bis (*2,4,6-trimethylanil*) (**2**) Ligand **2** was similarly prepared as described for ligand **1** from 2-hydroxy-5-methyl-isophthaldehyde and 2,4,6-trimethylaniline as yellow power in 73% yield. M.p. 155—156 ℃; ^{1}H NMR ($CDCl_3$) δ: 13.57 (s, 1H, ArOH), 8.49—8.53 (br, 2H, HC=N), 6.89 (s, 6H, ArH), 2.38 (s, 3H, $ArCH_3$), 2.27 (s, 6H, $ArCH_3$), 2.15 (s, 12H, $ArCH_3$); IR (KBr) ν: 3444 (br, m, OH), 2917 (s), 1630 (vs, HC=N), 1593 (m, HC=N), 1478 (s), 1462 (s), 855 cm^{-1}; EI-MS *m/z* (%): 398 (M^+, 9.9), 279 [($M^+ - C_6H_2(CH_3)_3$, 6.4), 265 [$M^+ - C_6H_2(CH_3)_3N$, 18.9], 264 [$M^+ - C_6H_2(CH_3)_3N - H$, 84.2], 146 [$C_6H_2(CH_3)_3N-(CH)^+$, 10.0]. Anal. calcd for $C_{27}H_{30}N_2O$: C 81.37, H 7.59, N 7.03; found C 81.24, H 7.68, N 6.87.

2,6-Diformyl-4-methylphenoxy-bis (*2,6-diisopropylanil*) (**3**) Ligand **3** was similarly prepared as described for ligand **1** from 2-hydroxy-5-methyl-isophthaldehyde and 2,6-diisopropylaniline. M.p. 165—166 ℃; ^{1}H NMR ($CDCl_3$) δ: 13.43 (s, 1H, ArOH), 8.17—8.59 (br, 2H, HC=N), 7.23 (s, 8H, ArH), 3.03—3.12 [m, 4H, $CH(CH_3)_2$], 2.48 (s, 3H, $ArCH_3$), 1.27 [s, 24H, $CH(CH_3)_2$]; IR (KBr) ν: 3427 (br, m, OH), 2962 (s), 1630 (vs, C=N), 1589 (vs, C=N), 1462 (vs), 1257 (vs), 1183 (vs), 1104 (m), 1038, 973, 761, 699 cm^{-1}; EI-MS *m/z* (%): 482 (M^+, 3.0), 307 {$M^+ - C_6H_3[CH(CH_3)_2]_2N$, 21.9}, 306 {$M^+ - C_6H_3[CH(CH_3)_2]_2N - H$, 100}, 292 {$M^+ - C_6H_3[CH(CH_3)_2]_2N - CH_3$, 5.0}. Anal. calcd for $C_{33}H_{42}N_2O$: C 82.11, H 8.77, N 5.80; found C 82.09, H 8.83, N 5.82.

2,6-Diformyl-4-methylphenoxy-bis (*3,5-dimethylanil*) (**4**) Ligand **4** was similarly prepared as described for ligand **1** using 2-hydroxy-5-methyl-isophthaldehyde with 3,5-dimethylaniline as a red powder in 97% yield. M.p. 161—162 ℃; ^{1}H NMR ($CDCl_3$) δ: 14.03 (s, 1H, ArOH), 8.83 (br, 2H, HC=N), 6.92 (s, 8H, ArH), 2.37 (s, 12H, $ArCH_3$), 1.61 (s, 3H, $ArCH_3$); IR (KBr) ν: 3441 (br, OH), 2917 (s), 1607 (vs, HC=N), 1580 (vs, HC=N), 1459 (s), 844, 687 cm^{-1}; EI-MS *m/z*: 370 (M^+, 89.9%), MS *m/z* (%): 369 ($M^+ - H$, 24.4), 355 ($M^+ - CH_3$, 6.7), 353 ($M^+ - OH$, 6.3), 266 [$M^+ - C_6H_3(CH_3)_2 + H$, 22.8], 265 ($M^+ - C_6H_3(CH_3)_2$, 100), 251 [$M^+ - C_6H_3(CH_3)_2 - N - H$, 12.2]. Anal. calcd for $C_{25}H_{26}N_2O$: C 81.05, H 7.07, N 7.56; found C 81.10, H 7.11, N 7.48.

{*2,6-Diformyl-4-methylphenoxy-bis* (*2,6-dimethylanil*)} $CoCl_2$ (**5**) To a solution of ligand **1** (150 mg, 0.41 mmol) in absolute ethanol (10 mL) with stirring under argon atmosphere at 50 ℃, a solution of $CoCl_2 \cdot 6H_2O$ (95 mg, 0.41 mmol) in absolute ethanol (10 mL) was added dropwise. After being stirred at 50 ℃ for 2 h, the solution was allowed to cool to room temperature. Then the solution was concentrated, and diethyl ether (10 mL) was added to precipitate the product as a green powder, which was subsequently washed with diethyl ether (3 × 5 mL), filtered and dried to afford (126 mg, yield 62%) deep green powder. The product was further recrystallized from mixture solvent of ethanol and diethyl ether. M.p. 152 ℃ (dec.); IR (KBr) ν: 3442 (br, OH), 2972 (m), 1634 (vs, C=N), 1592 (s), 1541 (vs), 1471 (s), 1233 (s), 1184, 775 cm^{-1}; FAB-MS *m/z* (%): 464 (M$^+$ − Cl), 371 (M$^+$ − $CoCl_2$). Anal. calcd for $C_{25}H_{26}N_2O \cdot CoCl_2$: H 5.24, N 5.60; found C 60.27, H 5.36, N 5.53.

{2, 6-*Diformyl-4-methylphenoxy-bis* (2,4,6-*trimethylanil*)} $CoCl_2$ (**6**) Prepared in the similar way as described for **5**, using ligand **2** and $CoCl_2 \cdot 6H_2O$, complex **6** was obtained in 61% yield. M.p. > 300 ℃; IR (KBr) ν: 3420 (br, m, OH), 2921 (m), 1634 (s, C=N), 1591 (m), 1541 (vs), 1479, 1069, 554 cm^{-1}; FAB-MS *m/z*: 492 (M$^+$ − Cl), 399 (M$^+$ − $CoCl_2$). Anal. calcd for $C_{27}H_{30}N_2O \cdot CoCl_2$: C 61.37, H 5.68, N 5.30; found C 61.05, H 5.60, N 5.30.

{2, 6-*Diformyl-4-methylphenoxy-bis* (2, 6-*diisopropylanil*} $CoCl_2$ (**7**) Prepared in the similar way as described above, complex **7** was obtained by the reaction of ligand **3** and $CoCl_2$ in 61% yield. M.p. > 300 ℃; IR (KBr) ν: 3422 (br, m), 2964 (vs), 1637 (vs), 1541 (vs), 1463 (s), 1230 (s), 801, 523 cm^{-1}; FAB-MS *m/z*: 576 (M$^+$ − Cl), 541 (M$^+$ − 2Cl), 482 (M$^+$ − $CoCl_2$). Anal. calcd for $C_{33}H_{42}N_2O \cdot CoCl_2$: C 64.71, H 6.91, N 4.57; found C 64.73, H 6.96, N 4.68.

{2, 6-*Diformyl-4-methylphenoxy-bis* (3, 5-*dimethylanil*)} $CoCl_2$ (**8**) Prepared in the similar way as described for **5**, complex **8** was obtained by the reaction of ligand **4** and $CoCl_2 \cdot 6H_2O$ in 76% yield. M.p. 242—243 ℃; IR (KBr): ν: 3424 (br, m, OH), 2918 (m), 1639 (vs, C=N), 1591(m), 1535 (vs), 1231, 1000, 849 cm^{-1}; FAB-MS *m/z*: 464 (M$^+$ − Cl), 428 (M$^+$ − 2Cl), 371 (M$^+$ − $CoCl_2$). Anal. calcd for $C_{25}H_{26}N_2O \cdot CoCl_2$: C 60.02; H 5.24; N, 5.60; found C 60.27, H 5.36, N, 5.53.

X-Ray crystallstructure determination of complex 6

Green crystal suitable for X-ray structure determination was grown from its dichloromethane-hexane (2∶1, *V*∶*V*) solution by evaporating at room temperature for two weeks. Single-crystal X-ray diffraction measurement was carried out at 293 K on a Bruker SMART 1000 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.071073 nm) using the ω-2θ scan mode. Unit cell dimensions were obtained with least-squares refinements in the range of 1.66°—25.03° and the structure was solved by direct method using the SHELXS-9714 and semi-empirical absorption correction (SSDABS) was applied. The final refinement was performed by full-matrix least-squares methods. H atoms were located by geometry and used in the structure-factor calculations. The crystal data, together with the data collection and structure refinement parameters are presented in Table 1. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center with the deposition number CCDC-187424, the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1 Crystal data and experimental details of complex **6**

Empirical formula	$C_{55}H_{60}Cl_6Co_2N_4O_2$
Formula weight	1139.63
Temperature	293(2) K
Crystal system	Monoclinic
space group	*C*2/*c*
a (nm)	2.2441(4)
b (nm)	1.5020(3)
c (nm)	1.7726(3)
β (°)	107.459(4)
V (nm^3)	5.6994(18)
Z	4
D_c (Mg/m^3)	1.328
F(000)	2360
Crystal size (nm)	0.10 × 0.05 × 0.05
R_1	0.0654,
wR_2	0.1182
R_1	0.2356,
wR_2	0.1568
No. reflections measured	11751 (total), 5032 (unique)
No. observed reflections	1597 [$I > 2\sigma(I)$]
Refinement method	Full-matrix least-squares

Results and discussion

Synthesis

The bis-schiff base ligands were prepared by the condensation of two equivalents of substituted aniline with one equivalent of 2,6-diformyl-4-methylphenol in ethanol. The complexes **5**—**8** were synthesized in reasonable yields by treating $CoCl_2 \cdot 6H_2O$ with the corresponding 2,6-bis(imino)phenoxy derivative ligands in ethanol at 50 ℃ (Scheme 1). The precipitates were collected by filtration and washed with ethyl ether. Complexes **5**—**8** are air-stable solids and insoluble in saturated hydrocarbons, while they are soluble in polar organic solvents, such as CH_2Cl_2, $CHCl_3$, ethanol, acetonitrile, *etc*.

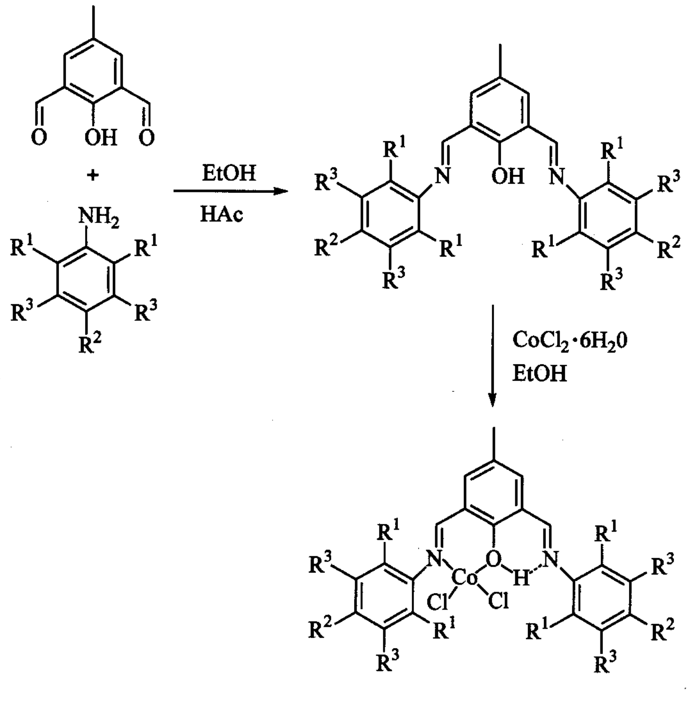
The ligands could be easily purified through re-crystallization in ethanol solution, and the elemental analysis data are in good agreement with formula. The ^1H NMR spectra of the Schiff base ligands show a single peak at about δ 13.43—14.03, which may be attributed to the presence of the intermolecular hydrogen bond between the phenolic group and the azomethine group at *cis* position. Additionally, a group of multiplet-signals corresponds to the aromatic protons at about δ 6.89—7.15. The infrared spectra of all the four ligands show two very strong absorption bands in the region of 1630—1580 cm^{-1} assigned to the carbon imine stretching mode, supporting the presence of Schiff-base linkage. A characteristic peak of hydroxyl group presents a broad band at 3440—3420 cm^{-1} and the mass spectrum shows reasonable peaks for their *m/z* and fragments.

The formation of Co(Ⅱ) complex may be due to the *para* position of the azomethine nitrogen and the hydroxyl, wherein coordination of both azomethine nitrogen atoms to the same metal atom is difficult. In Co(Ⅱ) complexes, the bands in the region of 1630—1580 cm^{-1} due to the azomethine group of the ligand undergoes a shift to lower frequency (1639—1535 cm^{-1}) upon complexation, indicating the coordination of azomethine nitrogen to cobalt atom along with another free azomethine group. The coordination of the phenoxy oxygen to the metal center in the complex is indicated by the shift of lower frequency of -OH group (3420—3442 cm^{-1}) compared with that of the free ligand (3441—3446 cm^{-1}). The elemental analysis data are in good agreement with formula. In addition to data presented above, the structure of the cobalt complex **6** was further confirmed by single crystal X-ray structure analysis.

Single crystal X-ray diffraction study

The structure of complex **6** is composed of two mononuclear centrosymmetrical with a solvent molecule CH_2Cl_2. The fragment structure perspective view of the half complex with the numbering scheme is shown in Fig. 1. Selected bond lengths and angles are given in Table 2.

Scheme 1 Schematic diagram for synthesizing ligands and their complexes



	R^1	R^2	R^3
1	Me	H	H
2	Me	Me	H
3	*i*-Pr	H	H
4	H	H	Me

	R^1	R^2	R^3
5	Me	H	H
6	Me	Me	H
7	*i*-Pr	H	H
8	H	H	Me

Table 2 Selected bond lengths (nm) and angles (°) for complex **6**

Bond lengths (nm) and angles (°)			
Co(1)—O(1)	0.1938(5)	Co(1)—N(1)	0.1993(6)
Co(1)—Cl(2)	0.2206(3)	Co(1)—Cl(1)	0.2239(2)
O(1)—C(17)	0.1316(8)	N(1)—C(10)	0.1316(8)
N(1)—C(6)	0.1463(9)	N(2)—C(18)	0.1306(8)
N(2)—C(19)	0.1440(9)		
O(1)-Co(1)-N(1)	92.5(2)	O(1)-Co(1)-Cl(2)	115.35(18)
N(1)-Co(1)-Cl(2)	112.81(19)	O(1)-Co(1)-Cl(1)	104.83(17)
N(1)-Co(1)-Cl(1)	123.05(19)	Cl(2)-Co(1)-Cl(1)	107.58(10)
C(17)-O(1)-Co(1)	124.5(5)	C(10)-N(1)-C(6)	114.0(6)
C(10)-N(1)-Co(1)	122.2(5)	C(6)-N(1)-Co(1)	123.5(5)
C(18)-N(2)-C(19)	122.8(7)		

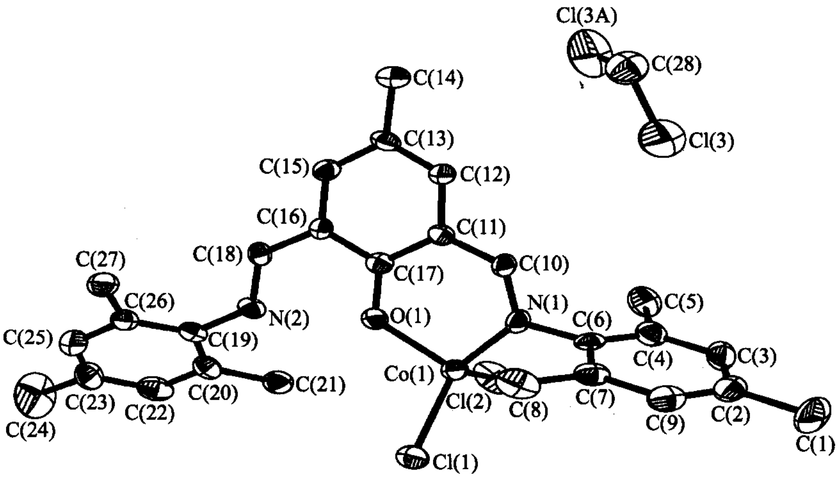


Fig. 1 Molecular structure of the complex **6** (hydrogens omitted for clarity).

The metal atom Co(II) is four-coordinated by one phenoxy oxygen atom, one imine nitrogen atom and two chlorine atoms. The geometry at the cobalt center can be described as distorted tetrahedral coordination geometry with chlorides located above or below the ligand plane. The distance of the Co(1)—Cl(1) [0.2239(2) nm] is a little longer than that of the Co(1)—Cl(2) [0.2206(3) nm], however, they are both shorter than the literature data (0.2251—0.2293 nm).[9] The Co(1)—N(1) (0.1993 nm) and Co(1)—O(1) (0.1938 nm) distances are also shorter than literature results[7] (0.2211 and 0.2226 nm, respectively). The C = N (uncoord.) distances, for instance, N(2)—C(18) (0.1306 nm) are relatively longer than the common distance 0.1265 nm,[15] and the C = N (coord.) distance [N(1)—C(6) 0.1316 nm] is much longer than that in coordinated Schiff base ligands [C = N 0.1298 nm].[2,12]

The N(1)-C(10)-C(11)-C(17)-O(1)-Co(1) formed a six-membered chelated ring with a mean deviation from plane 0.1171°, which is almost parallel co-planar to the phenyl ring with the dihedral angle of 14.5°, and oriented approximately orthogonal to the 2,4,6-trimethylphenyl ring C(2)-C(3)-C(4)-C(6)-C(7)-C(9) with *ca*. 81.2°. The bond angles at cobalt are in the range of 92.5(2)° to 123.05(19)°.

It is noteworthy to discuss the π-π intermolecular interactions. As shown in Figs. 2 and 3, centrosymmetrical related pairs of molecules have packed so that the plane face of uncoordinated 2,4,6-trimethylphenyl ring of one molecule is parallel to that of directed into the uncoordinated 2,4,6-trimethylphenyl ring of the adjacent molecule with a centroid distance 0.3357 nm and the dihedral angle of 18°. It is consistent with an aromatic-aromatic face-to-face interaction. Additionally, the phenoxy ring of one

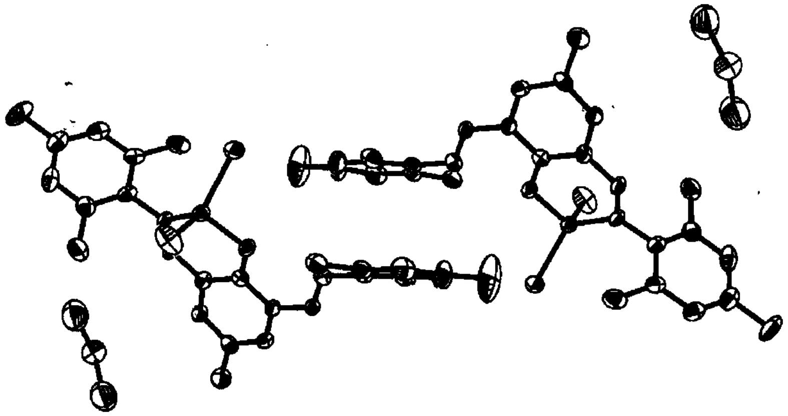


Fig. 2 π-π Stacking between the molecules.

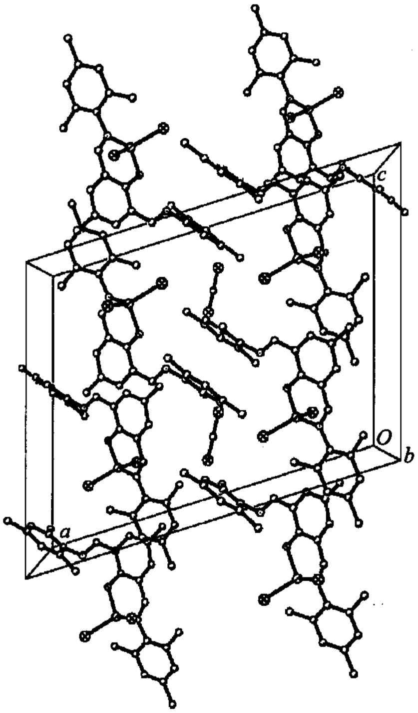


Fig. 3 Unit cell of the complex **6**.

molecule is parallel to the coordinated 2,4,6-trimethylphenyl ring of another adjacent molecule, with the dihedral angle of 8.7° and the distance 0.3865 nm. It is the result of intermolecular π-π interaction in the formation of two-dimensional wire-like coordination polymers.

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