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Synthesis of two novel cobalt complexes and their crystal structures

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Two new cobalt complexes were successfully synthesized from the reaction of binaphthyl Schiff base 2 with $Co(OAc)_2$ in the presence of sodium methoxide at 80 °C for 24 h and $Co(acac)_3$ in toluene under reflux. Their unique crystal structures are unambiguously disclosed by X-ray analysis. Complex 3 is triclinic, space group $P\bar{1}$, unit cell dimensions $a = 10.742(2)$ Å, $b = 11.153(2)$ Å, $c = 12.715$ Å, $\alpha = 79.865(3)°$, $\beta = 76.053°$, $\gamma = 72.532(4)°$, volume 1401.3(5) Å^3, $Z = 2$. Complex 4 is triclinic, space group $P\bar{1}$, unit cell dimensions $a = 10.801(2)$ Å, $b = 12.554(3)$ Å, $c = 15.219(3)$ Å, $\alpha = 105.672(4)°$, $\beta = 103.048°$, $\gamma = 104.594(4)°$, volume 1824.8(7) Å^3, $Z = 2$, calculated density 1.428 Mg m^{-3}. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: cobalt(II) complex; 1,1′-**binaphthyl-2,2′-diamine; binaphthyl Schiff base; crystal structure; X-ray analysis**

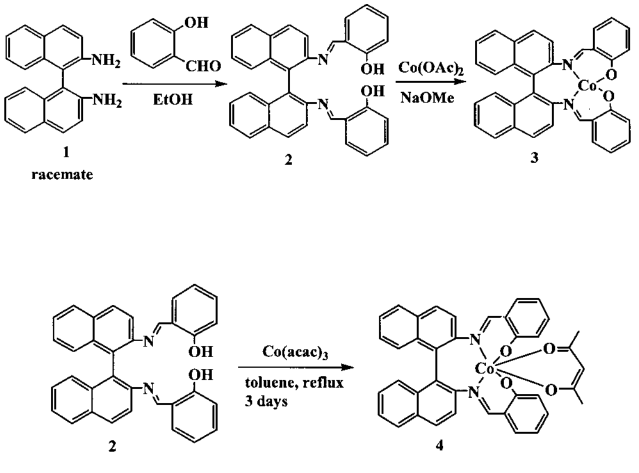
INTRODUCTION

Historically, metal complexes derived from 1,1′-binaphthyl-2,2′-diamine have been investigated for a long time because their chiral Schiff base complexes can catalyze asymmetric epoxidation of unfunctionalized alkenes.[1–3] So far, many crystal structures of binaphthyl Schiff base complexes with metals, such as Manganese(II),[4] Zinc(II),[5] Copper(II)[6] or Iron(III),[4] have been solved by X-ray analysis. Nevertheless, there is no report concerning the structure of a cobalt complex. Herein, we report the experimental details and the crystal structures of two new cobalt complexes **3** and **4** derived from a 1,1′-binaphthyl-2,2′-diamino Schiff base. The crystal structures of these two cobalt complexes have been unambiguously revealed by X-ray analysis.

RESULTS AND DISCUSSION

Synthesis of binaphthyl Schiff base 2 and its cobalt(II) (3) and cobalt(III) (4) complexes

The binaphthyl Schiff base **2** was synthesized according to the literature[7] and the cobalt(II) (**3**) and cobalt(III) (**4**) complexes were isolated by recrystallization from the reaction mixture of **1** with $Co(OAc)_2$ in the presence of sodium methoxide at 80 °C for 24 h and with $Co(acac)_3$ in toluene under reflux respectively (Scheme 1). The metal complex **3** was obtained as a red solid. We first confirmed its structure by microanalysis, because the cobalt(II) complex **3** is paramagnetic; therefore, its fine structure cannot be determined by ^1H NMR spectroscopic analysis. Complex **4**



Scheme 1.

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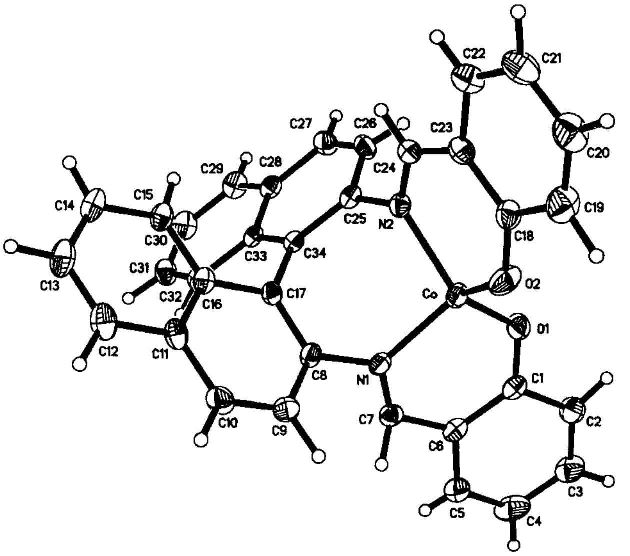

Figure 1. The crystal structure of **3**.

is diamagnetic; thus, its structure can be determined by ^{1}H NMR and microanalysis. In its ^{1}H NMR spectral data, two different methyl protons at δ 1.17 and 2.05 ppm, assigned to the acetylacetone (acac) group, were noted. The methine proton of the acac group was found at δ 5.33 ppm and the two olefinic protons of the imino group (HC=N) were assigned at δ 7.80 and 7.83 ppm. The rest belong to aromatic rings.

Molecular structures of complexes 3 and 4

Single crystals of the cobalt(II) (**3**) and cobalt(III) (**4**) complexes were obtained by careful recrystallization from 1:1 MeOH:CH_2Cl_2 and 1:1 THF:CH_3CH_2OH respectively. Then, their structures were unambiguously obtained by X-ray analysis (Figs 1 and 2). The crystal data for **3** and **4** are shown in Tables 1 and 2 respectively. The selected bond lengths and angles for **3** and **4** are shown in Tables 3 and 4 respectively.

From Fig. 1, it is clear that binaphthyl Schiff base **2** is a tetradentate ligand, because the two nitrogen atoms and the two oxygen atoms of the phenolic hydroxy group all coordinate to the metal center to form the metal complex. The bond lengths of the two Co—O bonds are essentially the same and the two Co—N bonds also have the same lengths. The dissymmetric binaphthyl group has a 70° dihedral angle. Thus, these binaphthyldiamino salen-type metal complexes have a sterically zigzag structure (not a planar structure).

As can be seen from Fig. 2, the binaphthyl Schiff base **2** reacts with Co(acac)$_3$ to form the octahedral metal complex **4**. The four coordinating atoms (two nitrogen atoms and two oxygen atoms) in binaphthyl Schiff base **2** and the two carbonyl groups from acac connect to the metal center to give

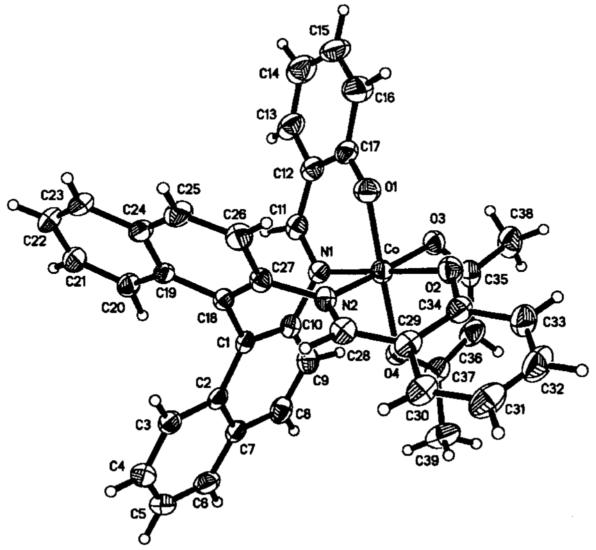

Figure 2. The crystal structure of **4**.

Table 1. Crystal data and structure refinement of **3**

Empirical formula	$C_{35}H_{26}CoN_2O_3$
Formular weight	581.51
Temperature (K)	293(2)
Crystal system	Triclinic
Lattice type	Primitive
Unit cell dimensions	
a (Å)	10.742(2)
b (Å)	11.153(2)
c (Å)	12.715(2)
α (deg)	79.865(3)
β (deg)	76.053(3)
γ (deg)	72.532(4)
V (Å^3)	1401.3(5)
Space group	$P\bar{1}$
Z value	2
D_{calc} (Mg m^{-3})	1.378
F(000)	602
θ range for data collection (deg)	1.66 to 25.50
Reflections collected/unique	7301/5081 (R_{int} = 0.0361)
Completeness to θ = 25.50 (%)	97.0
Absorption correction	Sadabs
Max. and min. transmission	1.0000 and 0.8053
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5081/1/455
Goodness-of-fit on F^2	1.110
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0703$, $wR_2 = 0.2386$
R indices (all data)	$R_1 = 0.0790$, $wR_2 = 0.2427$
Largest diff. peak and hole (e^- Å^{-3})	1.621 and − 0.430

this complex. The various bond lengths are: N_1—Co, 1.917 Å and N_2—Co, 1.934 Å; O_1—Co, 1.885 Å and O_2—Co, 1.893 Å; O_3—Co, 1.896 Å and O_4—Co, 1.896 Å. The dissymmetric binaphthyl group has a 66° dihedral angle. Its crystal packing showed that one molecule of THF, CH_3CH_2OH, and H_2O was included in its crystal structure (Fig. 3; ethanol and H_2O has been omitted). Interestingly, one hydrogen bond between THF and the imino group was realized with a distance of 2.541 Å (N=C—H···O) (Fig. 4). We have only found one example of this type of hydrogen bonding in the literature: a carboxylic acid with pyridine (Fig. 4) in which the C—H···O hydrogen bonding distance is 2.53(3) Å.[8,9] This result suggests that the hydrogen atom of the imino group in complex **4** was positively charged to some extent. This interesting electronic phenomenon may be due to the strong coordination of the imino group to the cobalt metal center. Further investigations on this aspect are under way.

CONCLUSION

In conclusion, we have prepared two novel cobalt complexes from the reaction of binaphthyl Schiff base **2** with $Co(OAc)_2$ in the presence of sodium methoxide at 80 °C for 24 h (**3**) and $Co(acac)_3$ in toluene under reflux (**4**). Their crystal structures are unambiguously revealed by X-ray analysis. We expect that our results will help towards a new strategy on the synthesis of chiral cobalt complexes that can be used for asymmetric oxidation. Further studies in this area are in progress in our laboratory.

Table 2. Crystal data and structure refinement of **4**

Empirical formula	$C_{45}H_{45}CoN_2O_7$
Formular weight	784.76
Temperature (K)	293(2)
Crystal system	Triclinic
Lattice type	Primitive
Unit cell dimensions	
a (Å)	10.801(2)
b (Å)	12.554(3)
c (Å)	15.219(3)
α (deg)	105.672(4)
β (deg)	103.048(4)
γ (deg)	104.594(4)
V (Å^3)	1824.8(7)
Space group	$P\bar{1}$
Z value	2
D_{calc} (Mg m^{-3})	1.428 g/cm^3
$F(000)$	824
θ range for data collection (deg)	1.46 to 28.44
Reflections collected/unique	11 081/8090 ($R_{int} = 0.0648$)
Completeness to $\theta = 28.44$ (%)	87.8
Absorption correction	Sadabs
Max. and min. transmission	1.0000 and 0.71887
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	8090/2/523
Goodness-of-fit on F^2	0.889
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0660$, $wR_2 = 0.1585$
R indices (all data)	$R_1 = 0.1180$, $wR_2 = 0.1759$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.595 and − 0.467

Table 3. Selected bond lengths (Å) and bond angles (deg) of **3**

Co—O2	1.886(4)
Co—O1	1.905(4)
Co—N2	1.978(4)
Co—N1	1.982(4)
O1—C1	1.327(7)
O2—C18	1.309(7)
O3—C36	1.327(12)
N1—C7	1.296(7)
N1—C8	1.437(7)
N2—C24	1.287(7)
N2—C25	1.437(6)
O2—Co—O1	114.54(19)
O2—Co—N2	95.28(18)
O1—Co—N2	127.60(19)
O2—Co—N1	128.3(2)
O1—Co—N1	94.32(17)
N2—Co—N1	99.56(17)
C1—O1—Co	124.3(4)
C18—O2—Co	125.5(4)
C7—N1—Co	123.1(4)
C8—N1—Co	116.2(3)
C24—N2—Co	122.8(4)
C25—N2—Co	117.6(3)

EXPERIMENTAL

General procedures

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were determined for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard on a Bruker AMX-300 spectrometer; J values are in hertz. IR spectra were determined using a Perkin–Elmer 983 spectrometer. Mass spectra were recorded with an HP-5989 instrument. High mass spectra were recorded on a Finnigan MA+ instrument. All solid compounds reported in this paper gave satisfactory CHN microanalyses with an Italian Carlo-Erba 1106 analyzer. Starting material **1** was prepared according to the literature.[10]

Typical reaction procedure for the preparation of binaphthyldiamino Schiff base 2[7]

A mixture of salicylaldehyde (0.21 g, 1.67 mmol) and

1,1′-binaphthyl-2,2′-diamine (0.2 g, 0.7 mmol) in ethanol (10 ml) was stirred at room temperature for 3 h. During the reaction, the corresponding diimine was precipitated as an orange solid. The crude product was filtered off, washed with ethanol and recrystallized from dichloromethane–diethyl ether to give a pure orange crystalline solid (0.28 g, 81%).

Table 4. Selected bond lengths (Å) and bond angles (deg) of **4**

Co—O1	1.885(3)
Co—O2	1.893(3)
Co—O4	1.896(3)
Co—O3	1.896(3)
Co—N1	1.917(3)
Co—N2	1.934(3)
O1—C17	1.315(5)
O2—C34	1.301(5)
O3—C35	1.270(5)
O4—C37	1.276(4)
O5—C41	1.663(16)
O6—C42	1.30(3)
O6—C45	1.542(19)
N1—C11	1.289(5)
N1—C10	1.437(5)
N2—C28	1.294(5)
N2—C27	1.443(4)
O1—Co—O	288.02(13)
O1—Co—O4	175.89(12)
O2—Co—O4	88.52(12)
O1—Co—O3	86.38(12)
O2—Co—O3	86.31(12)
O4—Co—O3	95.62(12)
O1—Co—N1	92.25(13)
O2—Co—N1	177.08(12)
O4—Co—N1	91.32(12)
O3—Co—N1	90.81(12)
O1—Co—N2	90.74(13)
O2—Co—N2	92.55(12)
O4—Co—N2	87.19(12)
O3—Co—N2	176.94(13)
N1—Co—N2	90.35(12)
C17—O1—Co	123.6(3)
C34—O2—Co	123.6(3)
C35—O3—Co	124.4(3)
C37—O4—Co	124.2(3)
C11—N1—Co	124.6(3)
C10—N1—Co	116.6(2)
C28—N2—Co	122.3(3)
C27—N2—Co	121.1(2)

Preparation of chiral cobalt(II) complex 3

Preparation of salen–cobalt complex:[11] to a solution of Schiff base (0.2 mmol) with sodium methoxide (0.4 mmol) under argon atmosphere in absolute ethanol (10 ml) was added 0.2 mmol Co(OAc)$_2$ and the resulting solution was heated at 80 °C for 24 h. After cooling, the precipitate was filtered off and washed with ethanol. The solid was dried under reduced pressure.

{[2,2′-[(1,1′-Binaphthalene)-2,2′-diylbis(nitrilomethylidyne)]-bis(phenolato)](2-)} cobalt(II) (**3**): a red solid; yield 64%. M.p. >200 °C. IR (film) ν 1605 cm^{-1} (C=N). EIMS *m/e* 549 (M$^+$). Anal. Found: C, 72.29; H, 5.00; N, 4.61. Calc. for $C_{34}H_{22}N_2O_2$·Co·C_2H_5OH: C, 72.60; H, 4.74; N, 4.70%.

A single crystal of **3** was obtained by recrystallization from 1:1 = MeOH:CH$_2$Cl$_2$. The crystal data of **1c**: empirical formula, $C_{35}H_{26}CoN_2O_3$; formula weight, 581.51; temperature, 293(2) K; wavelength, 0.710 73 Å; crystal system, triclinic; space group, $P\bar{1}$; unit cell dimensions, $a = 10.742(2)$ Å, $b = 11.153(2)$ Å, $c = 12.715$ Å, $\alpha = 79.865(3)$ °, $\beta = 76.053$ °, $\gamma = 72.532(4)$ °, volume 1401.3(5) Å^3; $Z = 2$; calculated density 1.378 Mg m^{-3}; $F(000)$, 602; max. and min. transmission, 1.0000 and 0.8053; final R indices $[I > 2\sigma(I)]$, $R_1 = 0.0703$, $R_w = 0.2386$. Its structure has been deposited at the Cambridge Crystallographic Data Centre and has been allocated the deposition number CCDC 178649.

Preparation of ({2,2′-[(1,1′-binaphthalene)-2,2′-diylbis(nitrilomethylidyne)]bisphenolato}-(2-))(2,4-pentanedionato)-cobalt(III) (4)

Co(acac)$_3$ (71 mg, 0.2 mmol) was added to a solution of **2** (98 mg, 0.2 mmol) in toluene (20 ml). The reaction solution was refluxed for 3 days under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel) to give **4** (98 mg, 73%) as a green solid (eluent was 1:2 ethyl acetate:petroleum ether v/v). m.p. 314–316 °C, IR (film) ν 1608 (C=N), 1587 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 1.17 (3H, s, Me), 2.05 (3H, s, Me), 5.33 (1H, s, CH), 6.32 (1H, t, $J = 7.5$ Hz, Ar), 6.40–6.45 (1H, m, Ar), 6.79 (1H, dd, $J = 7.8, 1.8$ Hz, Ar), 7.02–7.34 (13H, m, Ar), 7.43 (1H, t, $J = 7.5$ Hz, Ar), 7.48–7.54 (1H, m, Ar), 7.77 (1H, d, $J = 8.7$ Hz, Ar), 7.80 (1H, s, HC=N), 7.83 (1H, s, HC=N), 7.93(1H, d, $J = 8.4$ Hz, Ar); MS (EI) *m/z*: 549 (M$^+$ − acac) (95.16), 430 (M$^+$ − 119) (4.20), 342 (M$^+$ − 207) (8.69), 100 (M$^+$ − 449) (1.51). Anal. Found: C, 71.33, H, 5.06, N, 4.02. Calc. for $C_{39}H_{29}CoN_2O_4 \cdot 0.5H_2O$: C, 71.23, H, 4.60, N, 4.26%.

A single crystal of **4** was obtained by recrystallization from 1:1 = THF:CH$_3$CH$_2$OH. The crystal data of **4**: empirical formula $C_{45}H_{45}CoN_2O_7$ (one molecule of THF, ethanol and H$_2$O), formula weight, 784.76; temperature 293(2) K; wavelength, 0.710 73 Å, crystal system, triclinic; space group, $P\bar{1}$; unit cell dimensions, $a = 10.801(2)$ Å, $b = 12.554(3)$ Å, $c = 15.219(3)$ Å, $\alpha = 105.672(4)$ °, $\beta = 103.048$ °, $\gamma = 104.594(4)$ °, volume, 1824.8(7) Å^3; $Z = 2$; calculated density, 1.428 Mg m^{-3}, $F(000)$, 824; max. and min. transmission, 1.0000 and

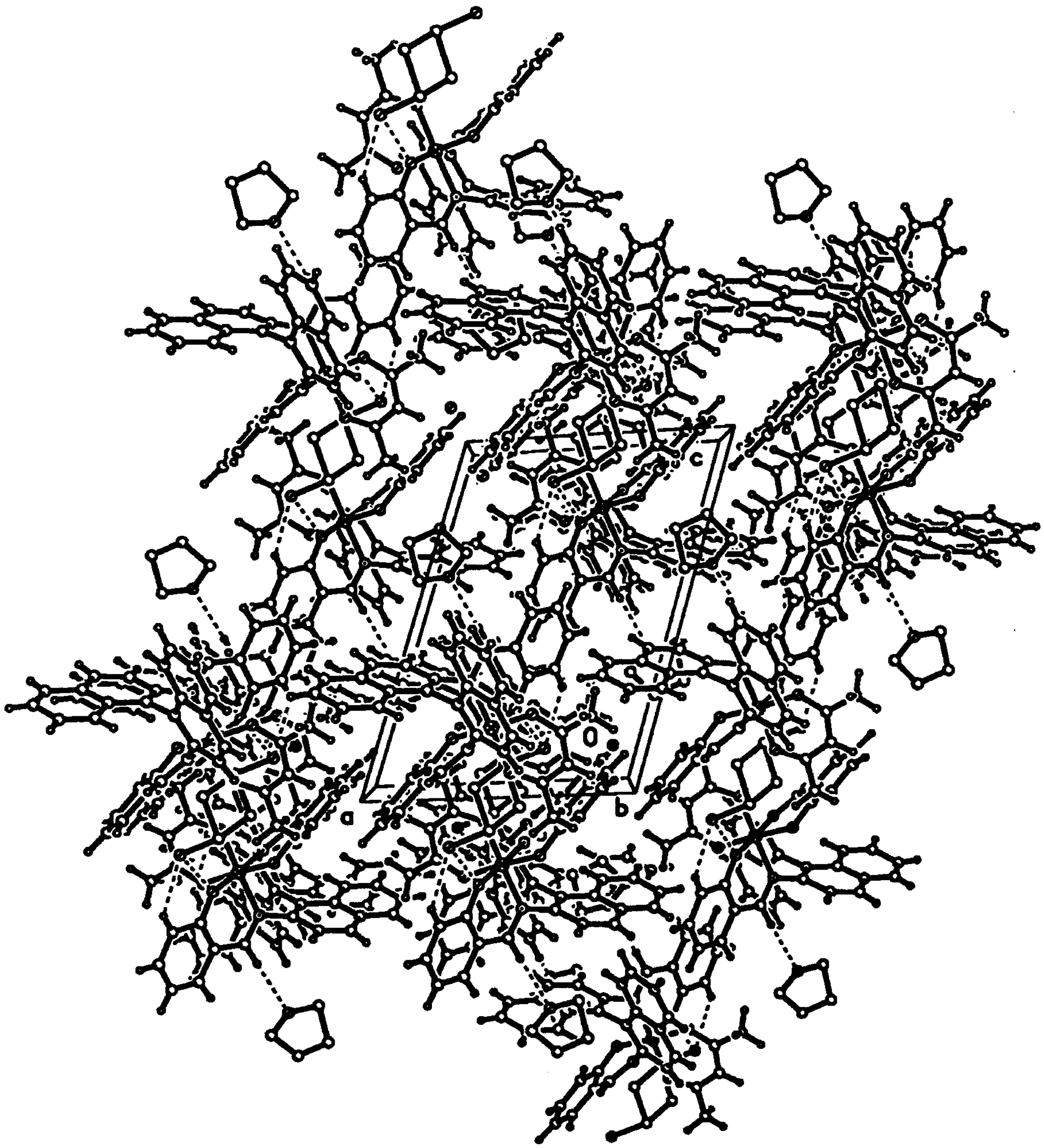

Figure 3. The crystal packing of **4**.

0.71887; final R indices $[I > 2\sigma(I)]$, $R_1 = 0.0660$, $R_w = 0.1585$. Its structure has been deposited at the Cambridge Crystallographic Data Centre and has been allocated the deposition number CCDC 191943.

Crystallography

A suitable crystal was mounted on the top of a glass capillary. Crystal data and details of data collection and structure refinement are given in Table 1. Data were collected on a CCD area detector with graphite-monochromated Mo Kα radiation $\lambda = 0.710\,69$ Å using the ω–2θ technique at 20 °C. A total of 3887 unique reflections was collected. The data were collected for Lorentz polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms

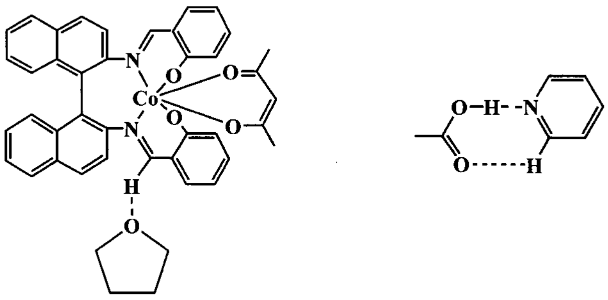

Figure 4. The hydrogen bonding between THF and imino group in complex **4**.

were included in calculated position. All calculations were performed using the SHELXS-97[12] crystallographic software package.

Acknowledgements

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