Structural characterization of nitro-substituted phenoxyiminato nickel complexes; inter-molecular π–π interactions in the solid states and effect of the electron drawing groups on catalytic activity

Dao Zhang, Linhong Weng, Guo-Xin Jin *

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, 200433 Shanghai, PR China

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ABSTRACT

Three phenoxyiminato nickel complexes [(L)Ni(PPh$_3$)(Ph)] have been prepared by the introduction of the electron drawing nitro substitutes on *ortho* or *para*-position of phenoxy and characterized by X-ray crystallography. Experimental and theory calculation suggested that the *ortho* and *para* nitro groups may be equally responsible for the small net charge on the central metal atoms because the interplanar angles between *o*-nitro planes and aromatic rings (28.7–37.3°) are much higher than those between *p*-nitro planes and aromatic rings (8.2–13.8°). In the solid states of these nickel complexes there exist the short inter-molecular π–π stacking interactions with the distances of 3.5828 Å (*ortho*-nitro), 3.5844 Å (*para*-nitro), and 3.0929 Å (*ortho*- and *para*-nitro) between two neighboring nitro-phenyl moieties.

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1. Introduction

Olefin polymerization by cationic complexes of d^8 metals (late transition metals) has been studied intensely in the last decade [1–6]. These catalysts are much more tolerant towards polar reagents in general by comparison to their highly oxophilic early transition metal counterparts. Thus, ethylene and 1-olefins can be copolymerized with electron-deficient vinyl monomers such as acrylates [7–10]. Grubbs and co-workers firstly reported a series of highly active neutral single-component phenoxyiminato based nickel catalysts for ethylene polymerization and copolymerization without any cocatalysts [11,12]. This discovery caused considerable interest, as it opened the chance to generate high-value products from cheap monomer supplies. The mechanism of ethylene polymerization by nickel phenoxyiminato catalysts has also been studied [13]. Until now, most studies still focused on the steric effect of this kind of neutral Ni(II) complexes, usually on the *ortho* position of phenol and imine. The degrees of polymer branching and thus crystallinity, high polymerization rates, and tolerance toward polar environments can be improved by this way [1–24].

Although the influence of electronic effect on catalytic of phenoxyiminato nickel(II) complexes [18], there have been a limited number of reports that describe the incorporation of electron drawing groups in the ligand "back-bone" [19–24]. Carlini et al. reported a Ziegler–Natta-type bis(nitro-substituted phenoxyiminato) nickel catalysts for homopolymerization of ethylene [19,22], styrene [23], norbornene [24] and methyl methacrylate (MMA) [20,21] with the methylalumoxane (MAO) or bis(1,5-cyclooctadiene)nickel(0) as cocatalysts. Herein, we report the introduction of nitro substitutes on the *ortho* and *para*-position of the phenol of the phenoxyiminato back-bone (Chart 1), as well as the synthesis and structural characterization of their nickel complexes. The electron drawing groups adds significantly to the net charge on nickels and thus has a major effect on catalytic activity of ethylene polymerization. In the solid states of these nickel complexes there exist the short inter-molecular π–π stacking interactions between two neighboring molecules.

2. Results and discussion

The nitro-substituted *o*-hydroxy-benzaldehyde was used as starting materials for preparation of the corresponding nitro-substituted phenol-imine *via* a straightforward Shiff-base condensation sequence. Ligands HL^1–HL^3 are light-yellow, yellow and orange–yellow solid which were treated with excess sodium hydride in THF to afford the corresponding sodium salts which react with nickel source *trans*-[NiPhCl(PPh$_3$)$_2$] to give complex **1–3** in 58–

* Corresponding author. Tel.: +86 21 65643776; fax: +86 21 65641740.
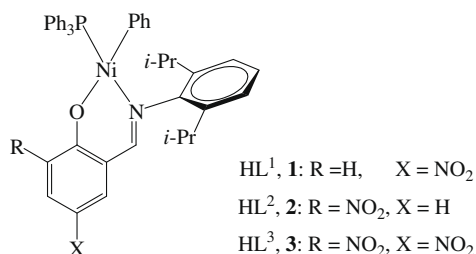   *E-mail address:* gxjin@fudan.edu.cn (G.-X. Jin).

Chart 1.

HL^1, **1**: R = H,   X = NO$_2$

HL^2, **2**: R = NO$_2$, X = H

HL^3, **3**: R = NO$_2$, X = NO$_2$

Table 1
Selected bond lengths (Å) and angles (°).

	1	2	3
Ni–O	1.9162(16)	1.901(3)	1.901(3)
Ni–N	1.9328(18)	1.942(3)	1.951(3)
Ni–P	2.1819(8)	2.1838(14)	2.1748(12)
Ni–C (Ph)	1.893(3)	1.896(4)	1.893(4)
C(Ph)–Ni–O	170.94(10)	164.09(16)	170.80(17)
C(Ph)–Ni–N	94.31(9)	95.57(16)	93.26(15)
O–Ni–N	90.29(7)	92.12(13)	92.38(13)
C(Ph)–Ni–P	90.87(8)	86.43(13)	85.31(12)
O–Ni–P	85.07(5)	88.19(10)	89.59(9)
N–Ni–P	173.70(6)	170.81(10)	175.51(11)

75% yield. Ligand HL^3 bearing two nitro groups is appraised to exhibit enhanced reactivity in certain instances. Complexes **1**–**3** were characterized by ^{1}H NMR and elemental analysis.

The crystals of **1**–**3** suitable for X-ray analysis were obtained as light-yellow platelet/orange red/dark-red block crystals, respectively, and sealed in the suitable glass capillary. The crystal structures of these nickel complexes are depicted in Fig. 1. The corresponding bond distances and angles are summarized in Table 1. For complexes **1**–**3**, the unit cell in the solid state contains two crystallographically independent, but chemically similar molecules that are related by a non-crystallographic pseudo-inversion center. And each molecule contains a phenoxyiminato chelating ligand, a triphenylphosphine and a phenyl group. The Ni atoms are arranged in a distorted square-planar geometry made up of four atoms of the ligand (P, O, N, C). The PPh$_3$ groups and the imine nitrogen atoms are *trans* to each other.

The most notable is the introduction of electron-withdrawing nitro groups that have obvious influence to the molecular structures (see Table 1). Firstly, the Ni–N [1.942(3) Å] and Ni–O [1.901(3) Å] bond distances of **2** bearing a nitro group in 3-position

are almost similar to those [1.9328(18) Å and 1.9162(16) Å, respectively] of **1** with a nitro group in 5-position within the range of experimental error. Secondly, complex **2** revealed a more twisted planar structure around nickel center than **1**. The *trans*- bond angle of C–Ni–O and N–Ni–P for complex **2** [**1**] are 164.09(16) [170.80(17)], 170.81(10) [175.51(11)]°, respectively. Thirdly, the Ni–N bond distance and O–Ni–P bind angle in complex **3** having two nitro groups in 3- and 5-positions further decrease to 1.9328(18) [1.951(3) for **1** and 1.942(3) Å for **2**] and 85.07(5) [89.59(9) for **1** and 88.19(10)° for **2**], which indicated the electron-withdrawing effect.

The packing diagrams for the isostructural compounds **1**–**3** are shown in Fig. 2, and the two molecules have strong inter-molecular π–π interactions. The π–π interaction type, distances and dihedral angles of the corresponding two parts were listed in Table 2 in which the intramolecular dihedral angles of nitro group with phenyl ring or another nitro group were also included. For complex **3**, the nitro group of Ni(1) molecule was almost parallel to phenyl
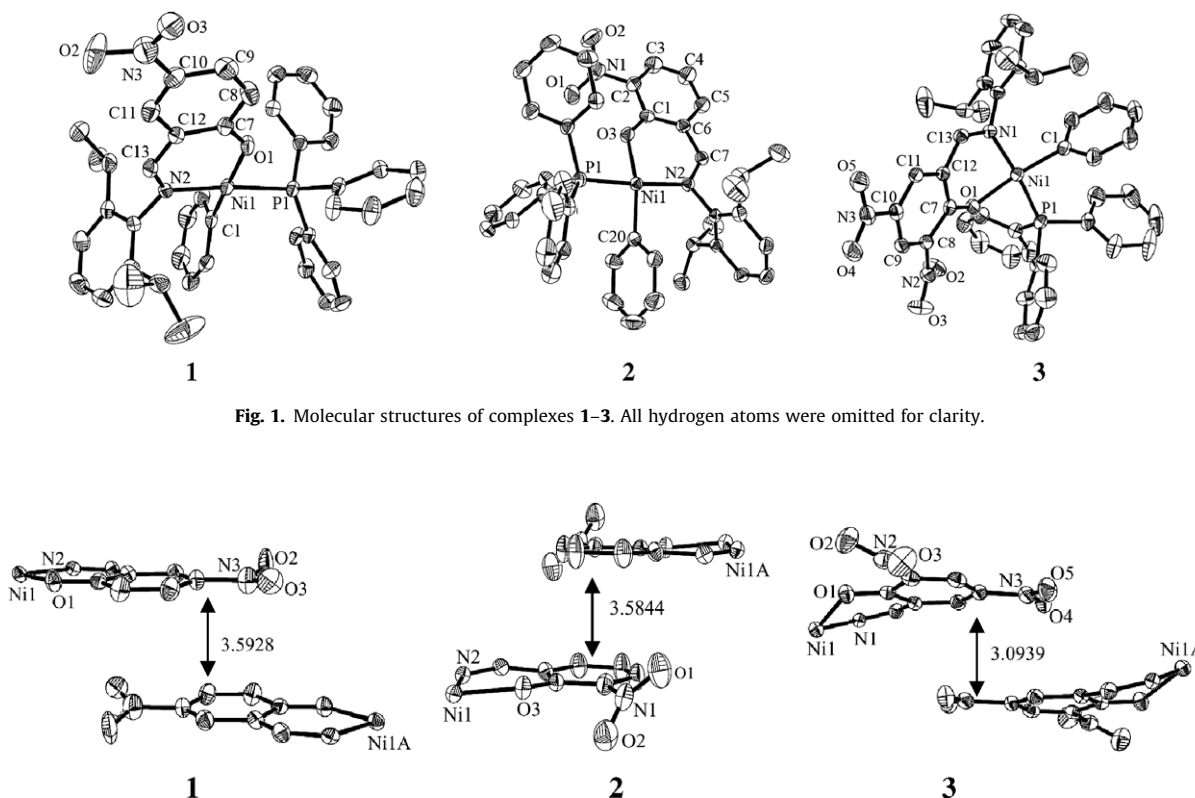

Fig. 1. Molecular structures of complexes **1**–**3**. All hydrogen atoms were omitted for clarity.

Fig. 2. The inter-molecular π–π stacking interactions between adjacent two phenoxyiminato ligands. The 2,6-^{i}Pr$_2$(C$_6$H$_3$) moieties, coordinated phenyl, PPh$_3$ groups, and all hydrogen atoms are omitted for clarity.

Table 2
Analysis of short inter-molecular π–π-interactions.[a]

Compound	π–π-Interaction type	$d_{\pi-\pi}$ (Å)	$\delta_{\pi-\pi}$ (°)	α (°)	β (°)	γ (°)
1	The phenyl ring···phenyl ring	3.5928	13.8	–	13.8	–
2	The phenyl ring···phenyl ring	3.5844	0	47.3	–	–
3	The nitro group···phenyl ring	3.0939	8.2	28.7	8.2	24.3

[a] Stacking parameters taken into account are $d_{\pi-\pi}$ (inter-molecular π–π-interaction distance), $\delta_{\pi-\pi}$ (angle between two inter-molecular π–π-interaction moieties), α (angle between *o*-nitro planes and aromatic ring), β (angle between *p*-nitro plane and aromatic ring), γ (angle between *o*-nitro planes and *p*-nitro planes).

Table 3
Result of polymerization of ethylene.[a]

Entry	Nickel (µmol)	T (°C)	Time (min)	Yield (g)	Activity [b]	M_v [c]
1	**1** (50)	60 ± 2	30	2.89	11.6	7000
2	**2** (44)	60 ± 2	30	3.24	14.7	54 000
4	**3** (68)	25 ± 2	120	1.62	1.19	108 000
5	**3** (44)	55 – 80	60	3.10	7.05	39 000
6	**3** (48)	95 ± 2	60	0.59	1.23	16 000
7	**3** (52)	60 ± 2	30	4.21	16.2	81 000
8	**3** (45)[d]	60 ± 2	30	0.90	4.00	42 000

[a] Polymerization conditions: 100 mL of autoclave, 50 mL of toluene, 10.0 atm of ethylene pressure.
[b] kg/(mol Ni h atm).
[c] Determined with Ubbelohde viscometer in dekalin at 135 ± 0.1 °C.
[d] Using 10 mL of toluene and 50 mL of hexane as polymerization solvent.

ring of Ni (1A) (the dihedral angle is only 8.2°), and the average distance is 3.0939 Å, which indicated that they have strong π–π interaction. However, complex **1** revealed different π–π stacking mode and the corresponding angle and average distance are 13.8° and 3.5928 Å, respectively (see Table 2), which was similar to complex **2** bearing weak π–π interaction in solid state. Moreover, for the three complexes two phenyl rings bearing nitro group of Ni(1) and Ni(1A) molecule are absolutely parallel to each other.

Nickel complexes **1–3** were tested for ethylene polymerization and the results were summarized in Table 3. Every polymerization without any activators such as Al-compounds or Ni(COD)$_2$. As expected, complexes **1–3** characterized by the presence of electron-withdrawing nitro groups on the phenoxyiminato ligand and of bulky isopropyl constituents on the N-aryl moiety, show much higher activities (Table 3). The position of nitro groups seems much sensitive to their catalytic behaviors. There is a clear increase in activity from **1** to **2** and **3** (Table 3, entries 1, 2 and 7). The molecular weights M_v and the number of methyl branches determined by high-temperature ^{13}C NMR spectra of the solid polymer are similar to those of the PEs produced using Grubbs catalysts (5–8 branches per 1000 carbon atoms) under similar conditions.

It has been reported that catalytic activity relied more on the electronic configuration of the catalyst in the ground state, especially the net charge on the central metal atom. The electron-withdrawing nature of nitro, which results in a more electrophilic metal center in the complexes, may increase the corresponding activity in the ethylene polymerization. The Q_{Eq} method calculation indicates the net charge on nickels in the complexes with nitro substitutes in *para* or *ortho* positions are 0.1431 (**1**) and 0.2646 (**2**),

Table 4
The net charge Q_{Eq} [e] of Ni, P, N, O atoms.

	1	2	3
Ni	−0.143116	−0.264609	−0.036006
P	0.665537	0.666157	0.62251
N	−0.48247	−0.508289	−0.474192
O	−0.589547	−0.605737	−0.545395
C	−0.061028	−0.151963	−0.031415

respectively (Table 4). Although nickel center in **1** has a more positive charge, the *ortho*-nitro groups of **2** are mostly close to the metal centers and act as more bulky groups to protect the active metal centers, which is responsible for the similar ethylene polymerization activity of **2** [14.7 kg/(mol Ni h atm)] and **1** [11.6 kg/(mol Ni h atm)]. Crystal structures of **1–3** also supported the result. The interplanar angles between *o*-nitro planes and aromatic rings (28.7–37.3°) are much larger than those between *p*-nitro planes and aromatic rings (8.2–13.8°).Compared with the complexes **1** and **2** with mono nitro substitute, the bis(nitro)-substituted complex **3** has relatively more positive nickel center and the net charge on Ni is – 0.0360. Thus the *ortho* and *para* nitro groups may be responsible for the small net charge on the central metal atoms besides bulky effect of *ortho* position.

3. Experimental

3.1. General considerations

All experiments with metal complexes were carried out under argon using standard Schlenk and vacuum-line techniques. Solvents were dried by refluxing with appropriate drying agents and distilled under argon prior to use. The commercially available reagents, 2,6-diisopropyl aniline (Aldrich Co.), NaH (60%, Aldrich Co.) were purchased and used without purification. The starting materials nitro-substituted 2-hydroxy-benzaldehyde, *trans*-[Ni(PPh$_3$)$_2$(Ph)Cl], phenoxyiminato ligand (HL^1–HL^3), and [(L)Ni(PPh$_3$)(Ph)] (**1–3**) were prepared according to the previously described methods [11,12,14–17]. Methylalumoxane (MAO) was purchased from Azko Nobel as a 7 wt% in toluene solution. ^{1}H NMR spectra were recorded on a Bruker DMX 500 spectrometer in C$_6$D$_6$ or CDCl$_3$. Elemental analysis was performed on an Elementar Vario EL III analyzer.

3.2. [(L^1)Ni(PPh$_3$)(Ph)] (**1**)

Ligand 5-nitro-N(2,6-diisopropylphenyl) phenol-imine (HL^1) was obtained as light-yellow solid in 79% yield. Anal. Calc. for C$_{19}$H$_{22}$N$_2$O$_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.01; H, 6.75; N, 8.62%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.20 (d, 12H, CH(CH$_3$)$_2$), 2.93 (septet, 2H, CH(CH$_3$)$_2$), 7.04–7.26 (m, 4H, H–Ar), 8.34–8.38 (m, 3H, CH=N + H$_p$–Ar$_{OH}$ + H$_m$–Ar$_{OH}$), 14.30 (bs, 1H, OH). Complex **1** was obtained as a yellow solid in 58% yield using a modified literature method [11]. Anal. Calc. for C$_{43}$H$_{41}$N$_2$NiO$_3$P: C, 71.39; H, 5.71; N, 3.87; Found: C, 71.37; H, 5.77; N, 3.89%. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.96 (d, 6H, J = 6.6 Hz), 1.22 (d, 6H, J = 6.6 Hz), 3.89 (sept., 2H, J = 6.6 Hz), 5.91–7.90 (m, 30H), 8.06 (s, 1H).

3.3. [(L^2)Ni(PPh$_3$)(Ph)] (**2**)

Ligand 3-nitro-N-(2,6-diisopropylphenyl) phenol-imine (HL^2) was obtained as orange–yellow solid in 86% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.20 (d, 12H, CH(CH$_3$)$_2$), 2.96 (septet, 2H, CH(CH$_3$)$_2$), 7.15–7.26 (m, 4H, H$_o$–Ar$_{OH}$ + H$_o$–Ar$_{iPr}$ + H$_m$–Ar$_{iPr}$), 7.21–7.26 (m, 3H, H$_p$–Ar$_{OH}$ + H$_m$–Ar$_{OH}$), 7.68 (d, 1H, Hp–Ar$_{NO_2}$),

Table 5
Crystallographic data.

	1	2	3
Empirical formula	$C_{43}H_{41}N_2NiO_3P$	$C_{43}H_{41}N_2NiO_3P$	$C_{43}H_{40}N_3NiO_5P$
Formula weight	723.46	723.46	768.46
Temperature (K)	293(2)	293(2)	293(2)
Crystal size (mm)	$0.10 \times 0.10 \times 0.08$	$0.15 \times 0.10 \times 0.08$	$0.20 \times 0.10 \times 0.05$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.592(2)	9.452(4)	11.715(3)
b (Å)	12.128(3)	11.548(5)	13.017(4)
c (Å)	16.091(4)	18.943(9)	14.951(4)
α (°)	90.915(4)	97.041(6)	84.227(4)
β (°)	97.916(3)	91.700(6)	67.431(4)
γ (°)	98.491(4)	113.392(6)	67.147(4)
V (Å³)	1832.3(8)	1876.4(15)	1936.8(9)
Z	2	2	2
D_τ (Mg/m³)	1.311	1.280	1.318
Absorbent coefficient (mm⁻¹)	0.615	0.601	0.591
$F(000)$	760	760	804
θ range (°)	1.28–25.01	1.09–25.01	1.48–25.01
Number of reflections collected/unique	7739/6366	7872/6490	8179/6740
	(R_{int} = 0.0450)	(R_{int} = 0.0255)	(R_{int} = 0.0207)
Number of data/restraints/parameter	6189/0/418	6490/0/451	6740/0/482
Goodness of fit (GOF) on F^2	0.937	1.053	0.827
Final R indices ($I > 2\sigma(I)$) [a]	0.0604, 0.1386	0.0536, 0.1392	0.0377, 0.0645
R indices (all data) [a]	0.1052, 0.1573	0.0793, 0.1524	0.0730, 0.0712
Largest difference peak and hole (e Å⁻³)	0.978/−0.353	0.463/−0.497	0.350/−0.199

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

8.16 (d, 1H, H_o–Ar_{NO_2}), 8.39 (s, 1H, CH=N), 14.96 (bs, 1H, OH). Anal. Calc. for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.01; H, 6.75; N, 8.62%. Complex **2** was isolated by filtration and washing with hexane as a dark-red solid in 72% yield. Anal. Calc. for $C_{43}H_{41}N_2NiO_3P$: C, 71.39; H, 5.71; N, 3.87. Found: C, 71.38; H, 5.74; N, 3.88%. ¹H NMR (500 MHz, C_6D_6): δ 1.08 (d, 6H, J = 6.6 Hz), 1.30 (d, 6H, J = 6.6 Hz), 4.05 (sept., 2H, J = 6.6 Hz), 6.06–7.85 (m, 30H), 8.09 (s, 1H).

3.4. [(L³)Ni(PPh₃)(Ph)] (3)

Ligand 3,5-dinitro-N-(2,6-diisopropylphenyl) phenol-dimine (HL³) was obtained as apricot-yellow solid in 91% yield. Anal. Calc. for $C_{19}H_{21}N_3O_5$: C, 61.45; H, 5.70; N, 11.31. Found: C, 61.41; H, 5.78; N, 11.37%. ¹H NMR (300 MHz, CDCl₃): δ 1.24 (d, 12H, CH(CH₃)₂), 2.96 (septet, 2H, CH(CH₃)₂), 7.29 (d, 2H, H_o–Ar_{iPr}), 7.39 (t, 1H, H_m–Ar_{iPr}), 8.31 (s, 1H, CH=N), 8.52 (d, 1H, H_o–$Ar_{CH=N}$), 9.06 (d, 1H, H_p–$Ar_{CH=N}$), 16.29 (bs, 1H, OH). Complex **3** was isolated as a dark-red solid in 75% yield. Anal. Calc. for $C_{43}H_{40}N_3NiO_5P$: C, 67.21; H, 5.25; N, 5.47. Found: C, 67.17; H, 5.24; N, 5.48%. ¹H NMR (500 MHz, C_6D_6): δ 0.98 (d, 6H, J = 6.6 Hz, CH(CH₃)₂), 1.16 (d, 6H, J = 6.6 Hz. CH(CH₃)₂), 3.84 (sept, 2H, J = 6.6 Hz, CH(CH₃)₂), 6.24 (m, 2H, J = 7.2 Hz, H_m–ArN=), 6.33 (m, 1H, J = 6.9 Hz, H_p–ArN=), 6.83 (m, 4H, J = 7.6 Hz, H–Ar), 6.93(m, 1H, J = 7.6 Hz, H–Ar), 7.02 (m, 9H, J = 7.4 Hz, H–Ar), 7.40 (d, 1H, J_{HH} = 8.2 Hz, H–Ar), 7.54 (t, 6H, J = 8.6 Hz, H–Ar), 7.73 (s, 1H, H–Ar), 8.23 (s, 1H, CH=N).

3.5. Ethylene polymerization

A 100-mL autoclave was charged with 40 mL of toluene under argon and the solution of the corresponding catalyst in toluene (10 mL) was added. After three times of ethylene gas exchange, ethylene pressure was raised to 10 atm and maintained for a certain time. The polymerization was terminated by the addition of methanol and dilutes HCl (10%). The solid polyethylene was filtered, washed with methanol and dried at 40 °C in vacuum.

3.6. Crystal structure determination

The single crystals suitable for X-ray analysis was sealed into a glass capillary and the intensity data of the single crystal were collected on the CCD Bruker Smart APEX system. Data obtained with the ω-2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package [25,26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. Crystallographic data are summarized in Table 5.

Supplementary material

CCDC 730606, 730607 and 730608 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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