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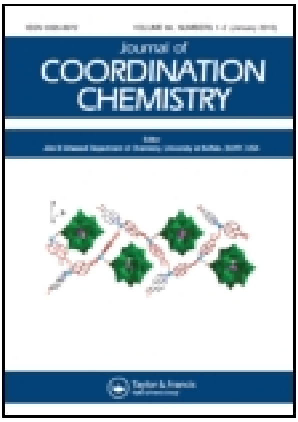

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Preparation of a series of NiL(η^2-C_{60}) complexes (L = 1,2-bis(diphenylphosphino)ethane, and 1,1′-bis(diphenylphosphino)ferrocene) by zinc dust reduction

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Accepted author version posted online: 07 Nov 2013.Published online: 07 Nov 2013.

To cite this article: Dmitri V. Konarev, Sergey I. Troyanov, Salavat S. Khasanov & Rimma N. Lyubovskaya (2013) Preparation of a series of NiL(η^2-C_{60}) complexes (L = 1,2-bis(diphenylphosphino)ethane, and 1,1′-bis(diphenylphosphino)ferrocene) by zinc dust reduction, Journal of Coordination Chemistry, 66:23, 4178-4187, DOI: 10.1080/00958972.2013.862618

To link to this article: http://dx.doi.org/10.1080/00958972.2013.862618

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 23, 4178–4187, http://dx.doi.org/10.1080/00958972.2013.862618

Preparation of a series of NiL(η^2-C_{60}) complexes (L = 1,2-bis(diphenylphosphino)ethane, and 1,1′-bis(diphenylphosphino)ferrocene) by zinc dust reduction

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(*Received 10 September 2013; accepted 25 October 2013*)

A simple method for preparation of nickel-fullerene coordination complexes has been developed. $NiLCl_2(Br_2)$ and C_{60} mixtures are reduced by zinc dust upon heating in *o*-dichlorobenzene. Diffusion of hexane into the reaction mixture results in formation of crystals of NiL(η^2-C_{60})·solvent (L = 1,2-bis(diphenylphosphino)ethane (dppe, **1**), 1,3-bis(diphenylphosphino)propane (dppp, **2**) and 1,1′-bis(diphenylphosphino)ferrocene (dppf, **3**)). Nickel coordinates to the 6–6 bonds of C_{60} by η^2- type and has distorted square-planar geometry. The average Ni–C(C_{60}) bond lengths are 1.936 (6)–1.977(3) Å. We found that increase in the P(L)–Ni–P(L) angle and the dihedral angle between the PNiP and CNiC planes results in elongation of the Ni–C(C_{60}) and Ni–P(L) bonds by 0.04–0.06 Å. Complexes **1–3** contain zero-valent nickel since fullerenes are neutral according to the IR- and visible-NIR spectra. Some of the IR-active bands of C_{60} are split into three bands in spectra of **1–3** due to C_{60} symmetry lowering, and the $F_{1u}(4)$ C_{60} mode is shifted to lower wave numbers due to the π-back donation. The formation of **1–3** is accompanied by appearance of new bands in the visible range at 435–447 and 661–680 nm.

Keywords: Fullerenes; Nickel; Coordination complexes; Crystal growth; Solid-state structures; IR and UV–vis spectroscopy

1. Introduction

The C_{60} molecule is formed by 60 identical carbon atoms bonded by two different type of C–C bonds. Shorter C–C bonds belonging to the hexagon ring junction behave as olefinic units and transition metal compounds coordinate to this bond by the η^2-type. Now, fullerene coordination complexes with platinum, palladium, nickel, chromium, iridium, osmium, and some other metals are known: $(R_3P)_2M(\eta^2\text{-}C_{60})$ (R = Et or Ph, M = Ni, Pd, Pt) [1–3], $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60})$ [4], $IrCOCl(R_3E)_2(\eta^2\text{-}C_{60}$, $C_{60}O$, C_{70} and $C_{84})$ [5–7], and others [8–11]. The formation of these complexes is accompanied by a substitution of one or two ligands in the coordination sphere of the transition metal by fullerene or an addition of

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Vaska's-type compounds $IrCOCl(R_3E)_2$ (E = P, As, R = alkyl or aryl) to the fullerene cage. Interest to the coordination transition metal-fullerene compounds is evoked by the analysis of the effects of metal coordination on chemical and physical properties of C_{60} as well as the design of functional fullerene compounds showing promising magnetic and photo-physical properties.

Metal-fullerene complexes can also be prepared by the reduction method. For example, it was supposed that the addition of $Co(CO)_4^-$, $Mn(CO)_5^-$ and $Re(CO)_5^-$ to C_{60} is realized through the fullerene reduction by an anionic carbonyl complex with the following η^2-addition of the $M(CO)_x^\bullet$ radical to the fullerene anions [12]. Transition metal fullerene complexes $M_2(\eta^5\text{-}C_5H_4CO_2Et)_2(\mu\text{-}C_{60})$ (M = Mo, W) were also obtained by the reaction of metal-coordination compounds with chemically generated $C_{60}{}^{2-}$ dianions [13]. Recently, we developed a new method for the preparation of metal-fullerene complexes by the reduction of $Ni(dppp)Cl_2$ and fullerenes C_{60} or C_{70} mixtures by sodium fluorenone or sodium tetraphenylborate, which allows the preparation of $\{Ni(dppp)(\eta^2\text{-}C_{60})\}\cdot 0.84C_6H_{14}\cdot 0.16C_6H_4Cl_2$ (**2**) and $\{Ni(dppp)(\eta^2\text{-}C_{70})\}\cdot 0.5C_6H_4Cl_2$ complexes (dppp is 1,3-bis(diphenylphosphino)propane) as single crystals. The analysis of the crystal structure of these complexes shows that the Ni–C(C_{60}) and Ni–C(C_{70}) bonds are the shortest M–C bonds among known metal-fullerene complexes [14, 15]. Recently, we modified our method to prepare cobalt-fullerene complexes by reduction of $Co(Ph_3P)_2Br_2$ and C_{60} mixture using sodium fluorenone and a few drops of benzonitrile. Under these conditions unusual dimers $\{Co(Ph_3P)(C_6H_5CN)\}_2(\mu_2\text{-}\eta^2,\eta^2\text{-}C_{60})_2$ were obtained which involved two neutral fullerene cages bridged by two zero-valent cobalt atoms bonded to fullerenes by the η^2-type. The Ph_3P and benzonitrile molecules additionally coordinate to the cobalt atoms [16].

In this work, we report on the development of the new very effective and simple reduction method for preparation of nickel-fullerene NiL·(η^2-C_{60}) complexes using available zinc powder as reductant. The method allows one to obtain and structurally characterize a series of coordination complexes of fullerene C_{60} with nickel coordinated to different diphosphine ligands. As a result, additionally to previously known $\{Ni(dppp)(\eta^2\text{-}C_{60})\}\cdot 0.84C_6H_{14}\cdot 0.16C_6H_4Cl_2$ (**2**), we obtained single crystals of two new complexes, $\{Ni(dppe)(\eta^2\text{-}C_{60})\}\cdot C_6H_4Cl_2$ (**1**) and $\{Ni(dppf)(\eta^2\text{-}C_{60})\}\cdot 0.5C_6H_4Cl_2\cdot 0.5C_6H_{14}$ (**3**), where dppe is 1,2-bis(diphenylphosphino)ethane and dppf is 1,1′-bis(diphenylphosphino)ferrocene. Diphosphine ligands bear different spacers between the phosphorus atoms (ethane, propane, or ferrocene). Therefore, the geometry around the nickel centers is slightly different in **1–3** allowing us to study how the nickel environment can affect the length of the nickel-carbon and nickel-phosphorus bonds with fullerene and diphosphine ligands, respectively. It has also been shown that coordination of nickel to fullerene is manifested in the IR- and visible-NIR spectra of the complexes.

2. Materials and methods

2.1. *Materials*

$Ni(dppe)Cl_2$, zinc dust, and 1,1′-bis(diphenylphosphino)ferrocene (dppf) were purchased from Aldrich. $Ni(dppf)Br_2$ was obtained by dissolving stoichiometric amounts of $NiBr_2$ and dppf in acetonitrile and stirring the solution at 60 °C for 4 h. The solution was cooled to room temperature, and brown green polycrystalline powder of $Ni(dppf)Br_2$ precipitated which was filtered off and dried under vacuum (95% yield). C_{60} of 99.98% purity was received from MTR Ltd. Solvents were purified in argon atmosphere. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure and hexane was distilled over Na/benzophenone. All manipulations for the synthesis of **1–3** were carried out in a MBraun 150B-G glove box with controlled inert atmosphere and the content of H_2O and O_2 less than 1 ppm. KBr pellets for IR- and UV–visible-NIR measurements were prepared in a glove box.

2.2. *Synthesis*

$\{Ni(dppe)(\eta^2\text{-}C_{60})\}\cdot C_6H_4Cl_2$ (**1**) and $\{Ni(dppf)(\eta^2\text{-}C_{60})\}\cdot 0.5C_6H_4Cl_2\cdot 0.5C_6H_{14}$ (**3**) were obtained by reduction of a stoichiometric mixture of $Ni(dppe)Cl_2$ (22 mg, 0.042 mM for **1**) or $Ni(dppf)Br_2$ (32.5 mg, 0.042 mM for **3**) and C_{60} (30 mg, 0.042 mM) in 14 mL of *o*-dichlorobenzene by an excess of zinc dust (160 mg) at 160 °C during 20 min in *o*-dichlorobenzene. The color of the solutions turned clear dark-green. The solutions were cooled to room temperature and stirred for 4 h. Then the solutions were filtered in a 50 mL glass tube 1.8 cm in diameter with a ground glass plug, and 30 mL of hexane was layered over the solution. The crystals of the complexes precipitated during one month were black plates for **1** and black prisms for **3**. The solvent was decanted off from the crystals and they were washed with hexane. Crystals with the size up to 0.4 × 0.4 × 0.6 mm^3 were obtained with 40–50% yield.

The composition of **1** and **3** was determined from X-ray diffraction on single crystal. Several crystals tested from the synthesis had the same unit cell parameters and belonged to one crystal phase.

The crystals of $\{Ni(dppp)(\eta^2\text{-}C_{60})\}\cdot$solvent (**2**) were obtained similarly. They show identical UV–visible-NIR and IR-spectra and are isostructural to the crystals described [14].

2.3. *General*

FT-IR spectra were measured in KBr pellets with a Perkin–Elmer 1000 Series spectrometer (400–7800 cm^{-1}). The visible-NIR spectra of the complexes were measured with a Perkin–Elmer Lambda 1050 spectrometer in the 300–2500 nm range.

2.4. *X-ray crystallographic study*

Crystal data for **1** at 120(1) K. $C_{92}H_{28}Cl_2NiP_2$, M_r = 1324.69 g M^{-1}, black plate, monoclinic, $P2_1/n$, a = 19.7363(14), b = 21.279(3), c = 26.236(3) Å, β = 94.079(7)°, V = 10,990 (2) $Å^3$, Z = 8, d_{Calcd} = 1.601 g cm^{-3}, μ = 0.569 mm^{-1}, $F(000)$ = 5376, $2\theta_{max}$ = 55.76°, reflections measured 32,501, unique reflections 32,420, reflections with $I > 2\sigma(I)$ = 24,645, parameters refined 1831, restraints 288, R_1 = 0.1114, wR_2 = 0.2604, GOF = 1.153. CCDC 945126.

Crystal data for **3** at 150(2) K. $C_{100}H_{37}ClFeNiP_2$, M_r = 1450.25 g M^{-1}, black prism, monoclinic, $P2_1/n$, a = 18.559(5), b = 16.323(5), c = 19.770(5) Å, β = 94.780(5)°, V = 5968(3) $Å^3$, Z = 4, d_{Calcd} = 1.614 g cm^{-3}, μ = 0.719 mm^{-1}, $F(000)$ = 2952, $2\theta_{max}$ = 58.72°, reflections measured 45,129, unique reflections 15,128, reflections with $I > 2\sigma(I)$ = 11,458, parameters refined 961, restraints 85, R_1 = 0.0532, wR_2 = 0.1682, GOF = 1.060. CCDC 943852.

X-ray diffraction data for **1** were collected at 120(2) K on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite-monochromated Mo-Kα radiation using an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out using CrysAlisPro, Oxford Diffraction Ltd [17]. The data for **3** were collected at 150(1) K on a Bruker Smart Apex II CCD with graphite-monochromated Mo-Kα radiation using a Japan Thermal Engineering Co. cooling system DX-CS190LD. Raw data reduction to F^2 was carried out using Bruker SAINT. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using SHELX-97 [18]. Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogens were calculated geometrically. The crystal structure of **1** was determined with somewhat higher R_1 value of 0.1114 due to twinning phenomena. Diffraction reflections from both twin domains were used in the structure refinement (SHELX HKLF5 file), the refined twin parameter in the studied crystal was 0.536(1). Two crystallographically independent solvent $C_6H_4Cl_2$ molecules in **1** are disordered between two orientations with the 0.607(7)/0.393(7) and 0.580(8)/0.420(8) occupancies. Totally 288 restraints were used for the refinement of crystal structure of **1**. Two hundred and seventy restraints (ISOR) concern ADP of the carbon atoms of fullerene cages (12 carbon atoms of either of two cages) and disordered dichlorobenzene molecules (21 atoms of 4 disordered components). Additional 18 restraints are due to the SAME instruction applied to the disordered dichlorobenzene molecules. Position of solvent molecules in **3** is shared by both $C_6H_4Cl_2$ and C_6H_{14} molecules with the 0.5/0.5 occupancies. Additionally, hexane is statistically disordered between two orientations. Totally 85 restraints were used for the refinement of crystal structure of **3**. The number of restraints results from the SHELXL instructions. The restraints are given for the severely disordered group of solvent molecules as FLAT instruction for $C_6H_4Cl_2$ and SADI instructions for two hexane molecules to keep the bond lengths and angles close to average values.

3. Results and discussion

3.1. *Synthesis*

The reduction route is suitable for preparation of nickel-fullerene complexes starting from a stoichiometric mixture of the corresponding $NiLCl_2$ salt and C_{60} at the addition of different reductants such as sodium fluorenone or sodium tetraphenylborate [14, 15]. As an available and effective reductant zinc dust was successively used for preparation of the salts with iron(I) phthalocyanine and iron(I) hexadecachlorophthalocyanine anions [19–21]. We found also that this reductant generates nickel-fullerene complexes in solution. The excess of zinc dust and a stoichiometric mixture of $NiLCl_2$ and C_{60} were stirred in *o*-dichlorobenzene at 160 °C during 20 min. After the solution turned green, it was cooled to room temperature and additionally stirred for 4 h. The diffusion of hexane into the obtained solution during one month provided precipitation of large well-shaped single crystals of $\{Ni(dppe)(\eta^2\text{-}C_{60})\}\cdot C_6H_4Cl_2$ (**1**) as black plates and $\{Ni(dppf)(\eta^2\text{-}C_{60})\}\cdot 0.5C_6H_{14}\cdot 0.5C_6H_4Cl_2$ (**3**) as black prisms (C_6H_{14}: hexane, $C_6H_4Cl_2$: *o*-dichlorobenzene). Crystals of **2** described in [14] can also be obtained using zinc dust as reductant instead of sodium fluorenone.

3.2. *Crystal structures*

There are two crystallographically independent $Ni(dppe)(\eta^2\text{-}C_{60})$ units in **1**, which slightly differ in geometry around the nickel centers (table 1), most probably due to different surrounding of the Ni(dppe) fragments. As a result, the P2NiC2 fragment is nearly planar in one unit and is twisted in the other unit (figures 1 and 2; table 1). Ni(dppe) coordinates to the 6–6 bond of C_{60} by η^2-type. The average Ni–C(C_{60}) bond lengths is 1.936(6) Å in Ni(dppe)(η^2-C_{60}) with planar P2NiC2 fragment. It is the shortest M–C bond among known η^2-complexes of fullerenes including previously described Ni(dppp) complexes with C_{60} and C_{70}. In the coordination units with a twisted P2NiC2 fragment, the Ni–C(C_{60}) bonds are slightly elongated to the average value of 1.952(6) Å. The Ni–P(dppe) distances are longer than the Ni–C(C_{60}) distances (table 1). The PNiP and CNiC angles are 89.13(8)–89.24(7)° and 44.48(6)–45.36(6)°, respectively, for both units. The C–C bonds to which the Ni atoms are coordinated are elongated up to 1.475(8)–1.485(9) Å in comparison with the average length of other C–C bonds in C_{60} (table 1). The reason of such bond elongation can be metal-to-C_{60} π-back-donation [1].

The crystallographically independent Ni(dppf)(η^2-C_{60}) unit in **3** has a planar P2NiC2 fragment with a very small dihedral angle between the PNiP and CNiC planes (table 1). The average Ni–C(C_{60}) bond length is 1.977(3) Å. The C–C bond of 1.490(4) Å which the Ni atom is coordinated to is noticeably longer than the average length of other C–C bonds in C_{60} (table 1). Geometry of the Ni(dppp)(η^2-C_{60}) units was described in [14].

Geometry of coordination units with planar P2NiC2 fragment is slightly changed in **1–3**. First of all, the P–Ni–P angle increases in the row: Ni(dppe)(η^2-C_{60}) < Ni(dppp)(η^2-C_{60}) < Ni(dppf)(η^2-C_{60}) from 89.24(7) to 106.33(3) Å (table 1). Most probably, different geometry of the bridge between the phosphorus atoms and the P–Ni–P angle affect average Ni–C(C_{60}) bond lengths since they are slightly elongated from 1.936(6) to 1.977(3) Å when the P–Ni–P angle increases by 17.1°. The average Ni–P(L) bond length also increases in this consequence from 2.142(2) up to 2.198(1) Å. Previously, it was noted that the Ni–P(L) bonds are slightly elongated in the row: Ni(dppm)Br_2 < Ni(dppe)Cl_2 < Ni(dppp)Cl_2, where dppm is 1,1-bis(diphenylphosphino)methane [22]. Obviously, the planarity of the P2NiC2 fragment can also affect Ni–C(C_{60}) bond lengths in **1** since at the same P–Ni–P angle of 89°, the Ni–C(C_{60}) bond is slightly elongated from 1.936(6) to 1.952(6) Å at transition from planar to twisted P2NiC2 fragment. On the whole, the geometry of the NiL(η^2-C_{60}) fragments in **1–3** is similar to that of Ni(dppe)Me_2 [23]. In the latter compound the average length of the Ni–C bonds of 1.982(2) Å is only slightly longer than those in the NiL(η^2-C_{60}) units of 1.936(6)–1.977(3) Å (table 1).

Table 1. Geometric parameters for NiL(η^2-C_{60}) coordination units in 1–3 (L = dppe, dppp and dppf) and in Ni(dppe)Me_2. Labels of atoms and angles are shown in figure 2.

	Ni(dppe)(η^2-C_{60})		Ni(dppp) (η^2-C_{60}) [8]	Ni(dppf) (η^2-C_{60})	Ni(dppe) Me_2 [23]
	Planar	Twisted	Planar	Planar	
Ni–C(C_{60}) bonds, Å	1.933(6)	1.949(6)	1.949(2)	1.967(3)	1.977(2)
	1.938(6)	1.954(6)	1.951(2)	1.987(3)	1.986(2)
Average value, Å	1.936(6)	1.952(2)	1.950(2)	1.977(3)	1.982(2)
Ni–P(L) bonds, Å	2.130(2)	2.139(2)	2.1523(5)	2.1858(9)	2.1536(9)
	2.153(2)	2.149(2)	2.1577(5)	2.2096(10)	2.1548(9)
Average value, Å	2.142(2)	2.144(2)	2.1550(5)	2.198(1)	2.1540(9)
η^2-coord. 6–6 C_{60} bond, Å	1.475(8)	1.485(9)	1.488(3)	1.490(4)	–
average 6–6 C_{60} bonds, Å	1.381(9)	1.386(12)	1.388(3)	1.389(4)	–
Angle P–Ni–P, °	89.24(7)	89.13(8)	100.67(2)	106.33(3)	87.23(4)
Angle C–Ni–C, °	45.36(6)	44.48(6)	44.87(2)	44.32(3)	87.31(12)
Dihedral angle between PNiP and CNiC planes, °	3.74(5)	12.71(5)	6.46(2)	1.15(3)	7.32(3)

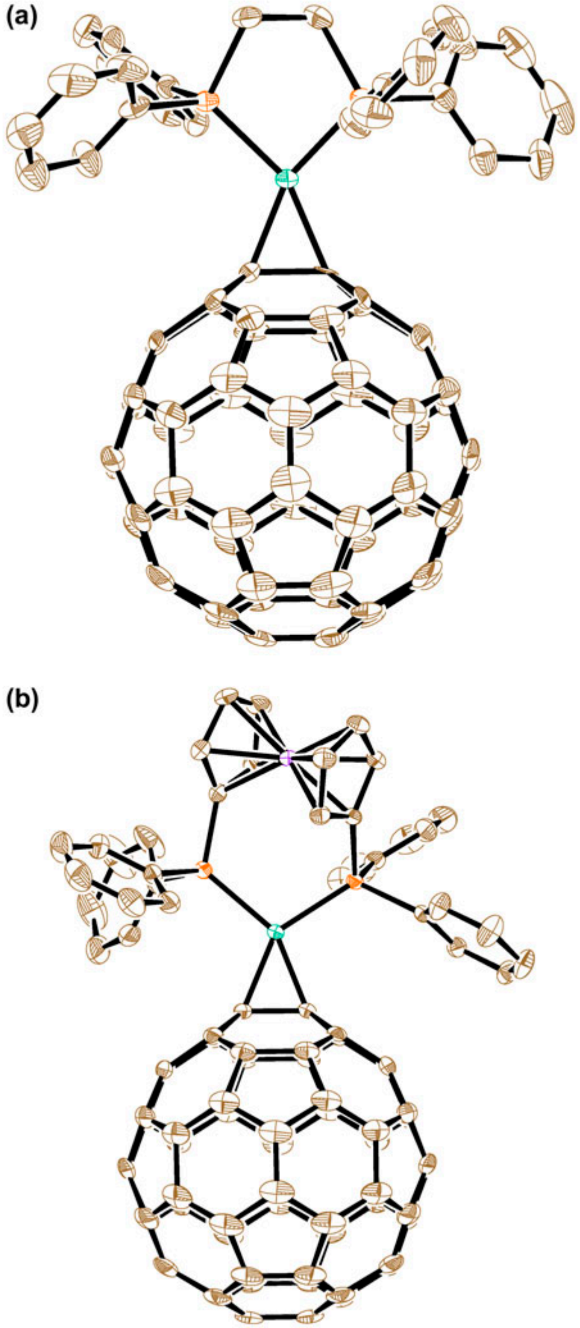

Figure 1. Molecular structure of Ni(dppe)(η^2-C_{60}) with planar P2NiC2 fragment (a) and Ni(dppf)(η^2-C_{60}) (b) coordination units. Ellipsoids have 50% probability.

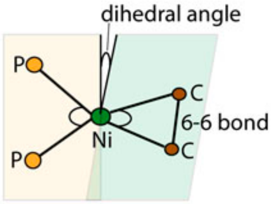

Figure 2. Label of atoms and angles for table 1.

{Ni(dppp)(η^2-C_{60})}·$0.84C_6H_{14}$·$0.16C_6H_4Cl_2$ (**2**) has layered structure in which fullerene layers alternate with the layers formed by bulky Ni(dppp) fragments. Each C_{60} has three neighbors in such layers with center-to-center interfullerene distances of 10.033–10.217 Å [14]. Packing motif of fullerene cages in **1** can be described as double columns in which each fullerene forms short van der Waals C…C contacts with four fullerene neighbors (figure 3(a)). Fullerenes are closely packed in such columns since center-to-center interfullerene distances are in the 9.84–9.91 Å range and each fullerene forms 12 van der Waals C…C contacts in the 3.00–3.37 Å range with the adjacent fullerenes. Transition to bulky Ni(dppf) group results in different packing of fullerene cages in **3**. They form distorted hexagonal packing with three neighbors for each fullerene cage (figure 3(b)). Center-to-center interfullerene distances of 10.03 Å in the layers are uniform and nine van der Waals C…C contacts in the 3.23–3.29 Å range are formed with the adjacent fullerene cages. Hexagonal vacancies formed by six fullerene cages in the fullerene layers are occupied by two Ni(dppf) groups and solvent molecules.

3.3. *IR- and UV–visible spectra of the complexes*

The IR-spectrum of fullerene noticeably changes at the formation of **1** and **3**. Degenerated F_{1u}(1–4) modes are positioned as single bands in the spectrum of starting C_{60} at 526, 576, 1182, and 1429 cm^{-1}, respectively (see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.862618). Only F_{1u}(3) mode of C_{60} remains unsplit in spectra of the complexes, whereas the F_{1u}(1), F_{1u}(2), and F_{1u}(4) modes in the spectrum of **1** and the F_{1u}(1) mode in the spectrum of **3** are split into three bands due to the C_{60} symmetry lowering at the nickel coordination. It is known that the F_{1u}(4) mode of C_{60} is sensitive to charge transfer to the C_{60} molecule and is shifted from 1429 cm^{-1} in the neutral state to 1396–1388 cm^{-1} in the radical anion state [24–26]. The absorption bands of this mode are manifested at 1410, 1416, and 1420 cm^{-1} in the spectrum of **1** and at 1418 cm^{-1} in the spectrum of **3**. Therefore, they are noticeably shifted to the lower frequencies as compared with its position in the spectrum of starting C_{60} (1429 cm^{-1}). The observed shift can be due to the π-back-donation [1]. Previously, similar effects were found in the Raman spectra of the $(PR_3)_2M(\eta^2\text{-}C_{60})$ complexes (M = Ni, Pd and Pt) [27].

The spectra of **1** and **3** in the UV–visible-NIR range are shown in figure 4. Complex **1** shows major bands in the visible range at 447 and 680 nm and **3** at 337, 435, and 661 nm. Bands at 435–447 and 661–680 nm are typical for fullerene coordination complexes. Similar bands are observed in the solution spectra of $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60})$ at 448

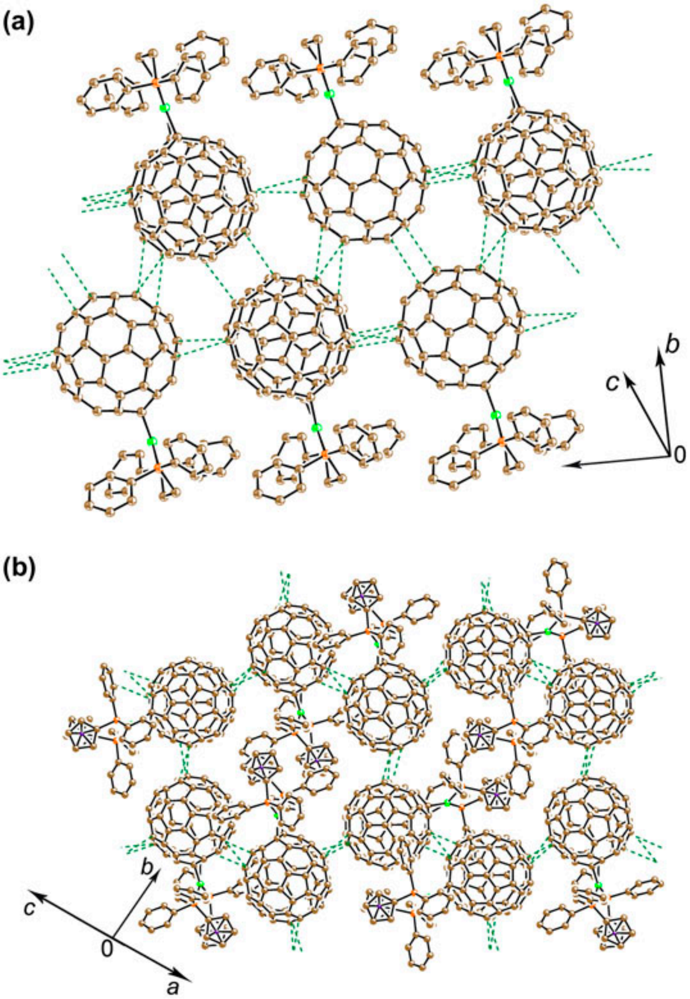

Figure 3. Packing of the Ni(dppe)·(η^2-C_{60}) units in **1** (a) and the Ni(dppf)·(η^2-C_{60}) units in **3** (b). Solvent molecules are not shown for clarity. Short van der Waals C…C contacts between fullerenes are shown by green dashed lines (see http://dx.doi.org/10.1080/00958972.2013.862618 for color version).

and 650 nm [4] and an addition product of $H_3Ir(PPh_3)_3$ at 435 and 650 nm [28]. A low-energy band can be attributed to intramolecular charge transfer in the coordination metal-C_{60} units [29, 30]. The bands in the NIR range attributed to the $C_{60}^{\bullet-}$ radical anions at 1070–1080 nm [31–33] are not observed in spectra of **1** and **3** showing the absence of noticeable electron density transfer from nickel to the C_{60} cage. The EPR spectra of **1** and **3** measured in anaerobic conditions show only a weak narrow signal with g = 2.0000–2.0002, which at room temperature does not exceed 0.2% of spins from total amount of C_{60}. This signal is similar to that observed previously in **2** [14]. Therefore, **1–3** are EPR silent and do not contain unpaired spins. Therefore, the obtained complexes are molecular ones and contain neutral fullerene C_{60} and zero-valent nickel atoms.

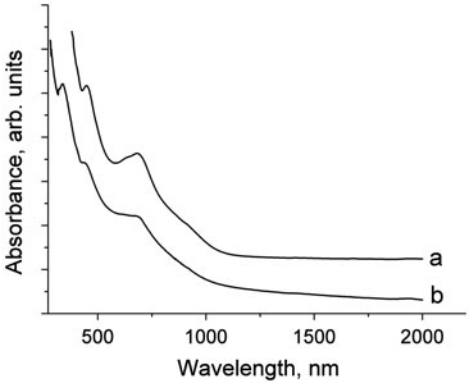

Figure 4. UV–visible-NIR spectra of **1** (a) and **3** (b) measured in KBr pellets in anaerobic conditions.

4. Conclusion

In this work we showed that nickel-fullerene complexes are generated in solution by reduction of $NiLCl_2$ and C_{60} mixtures by zinc dust. As a result, nickel-fullerene coordination complexes $NiL(\eta^2\text{-}C_{60})\cdot$solvent (**1–3**) (L = dppe, dppp, and dppf) were obtained as single crystals. The average Ni–C(C_{60}) bond lengths in 1–3 are the shortest M–C bonds among known metal-fullerene complexes. These bonds are even shorter than the Ni–C bonds in Ni (dppe)Me_2. Different lengths of bridges in dppe, dppp, and dppf increase the P(L)–Ni–P(L) angle and elongate the Ni–C(C_{60}) and Ni–P(L) bonds by 0.04–0.06 Å. The dihedral angle between the PNiP and CNiC planes also affects the Ni–C(C_{60}) bond length. Some of the IR-active bands of C_{60} are split into three bands in spectra of **1–3** due to the C_{60} symmetry lowering. The $F_{1u}(4)$ C_{60} mode is shifted to smaller wave numbers due to the π-back donation. The formation of **1–3** is accompanied by the appearance of new bands in the visible range.

Funding

This work was supported by RFBR-JSPS (Japan – Russia Research Cooperative Program) [grant number 12-03-92107].

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