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PAPER

Preparation of η^2 -complexes of fullerenes by reduction. Crystal structure and optical properties of $\{Ni(dppp)\cdot(\eta^2-C_{70})\}\cdot(C_6H_4Cl_2)_{0.5}$

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The new reduction method for preparation of η^2 -complexes of fullerenes

with nickel–1,3-bis(diphenylphosphino)propane has been developed in which Ni(dppp)Cl₂ and $C_{60}(C_{70})$ mixtures are reduced with sodium tetraphenylborate. Single crystals of the first η^2 -complex of nickel with fullerene C_{70} : {Ni(dppp)·(η^2 - C_{70})}·($C_6H_4Cl_2$)_{0.5} (1) ($C_6H_4Cl_2$ = *o*-dichlorobenzene) have been obtained as well as the previously described complex with fullerene C_{60} : {Ni(dppp)·(η^2 - C_{60})}·(Solvent) (2). The crystal structure of 1 has been solved to show the coordination of nickel to the C–C bond of C_{70} at the 6–6 ring junction of η^2 -type to form Ni–C(C_{70}) bonds of 1.929–1.941(2) Å length, the shortest M–C bonds among those known for η^2 -complexes of fullerenes C_{60} and C_{70} . The length of the C–C bond to which Ni atom is coordinated (1.494(3) Å) is noticeably longer than the average length of these bonds in C_{70} (1.381(2) Å). Optical spectra of 1 in the IR- and UV-visible ranges have been analyzed to show the splitting of some C_{70} bands due to C_{70} symmetry lowering. The complex has a red–brown color in solution and manifests three bands in the visible range at 379, 467 and 680 nm. The solution of 1 is air sensitive since air exposure restores the color and absorption bands of the starting C_{70} at 383 and 474 nm.

Introduction

Fullerenes C_{60} and C_{70} contain several types of C–C bonds. Shorter C–C bonds at the 6–6 ring junction behave as olefinic units and transition metal compounds can coordinate to them by η^2 -bonding. As a result, fullerenes form a variety of transitionmetal complexes bonded by M–C coordination bonds.¹⁻¹⁵ Those were mainly prepared with C_{60} ,¹⁻⁷ whereas relatively fewer such complexes, among them complexes with platinum, palladium, molybdenum and iridium, are known for C_{70} .⁸⁻¹³ Several complexes of C_{70} were structurally characterized as multiaddition products such as $(\eta^2, \eta^2 - C_{70}) \cdot \{(Me_2PhP)_2IrCOCl\}_2^{14}$ and $(\eta^2, \eta^2, \eta^2, \eta^2, \Gamma_{70}) \cdot \{(Ph_3P)_2Pd\}_4$.¹⁵ No coordination complexes of nickel with fullerene C_{70} are known.

Generally, zerovalent compounds of nickel, platinum, palladium, molybdenum, chromium and some other metals are used for the preparation of fullerene coordination complexes, for example, $(Ph_3P)_2M(\eta^2-C_2H_4)$ (M = Pd, Pt), $(R_3P)_4M$ (R = Et or Ph, M = Ni, Pd, Pt) and others. Upon reaction the fullerene substitutes one or two ligands in the coordination sphere of the transition metal.¹⁻⁶ Another way of preparing fullerene coordination complexes is addition of Vaska-type compounds $IrCOCl(R_3E)_2$ (E = P, As, R = alkyl or aryl) to fullerenes.⁷

Compounds containing positively charged metals coordinating phosphine ligands are another wide family of metal complexes.¹⁶ They can easily be prepared by the interaction of metal salts of different metals (Ni²⁺, Co²⁺, Fe²⁺ and etc.) with phosphine ligands. We developed a reduction method for preparation of η^2 -coordination complexes of fullerenes with nickel starting from (Ni(dppp)Cl₂) (dppp = 1,3-bis(diphenylphosphino)propane). Sodium fluorenone was used as a reductant and the nickel-containing fullerene complex {Ni(dppp)· $(\eta^2$ -C₆₀)}·(Solvent) (2) was obtained as single crystals and structurally characterized.17 As sodium fluorenone is extremely air-sensitive, and all manipulations with this reductant require strictly anaerobic conditions, we thus searched for a more convenient reductant to prepare nickel-fullerene coordination complexes. It was shown^{18,19} that air-stable sodium tetraphenylborate (NaBPh₄) reduces C₆₀ in a tetrahydrofuran-chlorobenzene mixture producing ionic $(M^+)_x \cdot (THF)_y \cdot (C_{60}^-)$ (x = 0.39, y = 2.2; M = Li, Na, K) complexes. This reagent can also be used to generate nickel-fullerene coordination complexes for both C₇₀ and C₆₀. The reaction of a stoichiometric mixture of fullerene (C₇₀ or C₆₀) and Ni(dppp)Cl₂ with two equivalents of NaBPh₄ (1:1:2 molar ratio) in o-dichlorobenzene (C₆H₄Cl₂) yielded redbrown and green solutions, respectively. Single crystals of the coordination complexes can be obtained from the solutions by slow diffusion of hexane. $\{Ni(dppp) \cdot (\eta^2 \text{-} C_{70})\} \cdot (C_6H_4Cl_2)_{0.5}$ (1) is the first η^2 -complex of nickel with fullerene C_{70} and here we discuss its crystal structure and optical properties. The crystals of ${Ni(dppp) \cdot (\eta^2 - C_{60})} \cdot (Solvent)$ (2) were isostructural to those of

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previously described {Ni(dppp)·(η^2 -C₆₀)}·(C₆H₁₄)_{0.84}·(C₆H₄Cl₂)_{0.16} (C₆H₁₄ = hexane) obtained by the reduction of Ni(dppp)Cl₂-C₆₀ mixture with sodium fluorenone.¹⁷

Results and discussion

The crystal structure of 1 was determined at 130(2) K and the complex has a triclinic unit cell. The Ni(dppp) \cdot (η^2 -C₇₀) units are well ordered, whereas solvent C₆H₄Cl₂ molecules are statistically disordered between two orientations. Ni(dppp) coordinates to the C-C bond of C₇₀ at the 6-6 ring junction (Fig. 1). The bond is similar to the 6–6 bonds of C_{60} . Coordination is realized by η^2 -attachment to form two slightly different Ni–C(C₆₀) bonds of lengths 1.927(2) and 1.940(2) Å. These bonds are even shorter than the length of the Ni–C bonds in 2 $(1.948-1.951(2) \text{ Å})^{17}$ and other known η^2 -complexes of C₆₀ and C₇₀ fullerenes. According to CCDC database the following lengths of the M-C bonds were found for η^2 -coordination complexes of fullerene C₇₀: 2.11–2.12 Å for Pd, 2.07-2.15 Å for Pt, 2.11-2.20 Å for Ir and 2.27-2.30 Å for Mo.⁸⁻¹⁵ The Ni-P(dppp) distances are noticeably longer (2.1436(6) and 2.1519(6) Å) than the Ni–C(C_{70}) distances, and the PNiP and CNiC angles are 99.06(2) and 45.41(8)°, respectively. The C-C bond length (1.491(3) Å) where Ni atom is coordinated is noticeably longer than the average length of these bonds in C_{70} (1.381(2) Å) and is probably caused by metal-to- C_{70} π -back-donation.¹ Similar elongation of the C-C bonds is observed at the formation of various coordination (ML) $(\eta^2 - C_{70})$ units (1.460–1.522 Å).8-15 The Ni coordination geometry is planar since all five atoms (nickel, two C₇₀ carbon and two phosphorus atoms bonded to nickel) are nearly coplanar with a maximum deviation of 0.011 Å from the least-square plane. As a whole, the geometry of the Ni(dppp) \cdot (η^2 -C₇₀) units is similar to that of the Ni(dppp)·(η^2 -C₆₀) units¹⁷ and the theoretically predicted geometry of the $(PH_3)_2Ni \cdot (\eta^2 - C_{60})$ units (predicted length of the Ni–C(C₆₀) bonds is 1.989 Å).20

Fullerene C_{70} coordinates to metals by C–C bonds at the 6–6 ring junction^{8-13} and even multiaddition to C_{70} is realized



Fig. 1 Molecular structure of the Ni(dppp) \cdot (η^2 -C₇₀) unit.

in such a way that bonds of this type only are involved in coordination.^{14,15} Moreover, dimerization of the C_{70} .⁻ radical anions²¹⁻²³ and polymerization of the C_{70} .²⁻ dianions^{24,25} in ionic compounds are also realized by carbon atoms involved in these bonds. Thus, the C–C bonds at the 6–6 ring junction in C_{70} are most active in coordination, dimerization and polymerization of fullerene C_{70} . Indeed, the Hückel molecular orbital calculations showed²⁶ that these bonds have one of the highest π -bond orders among different C–C bonds of C_{70} .

Fullerene C_{70} forms distorted hexagonal layers in **1** with six neighbors for each C_{70} (Fig. 2a). Distances between the center of mass of fullerene C_{70} are 10.561 Å along the [100] direction and 10.012 Å along the [001] direction (with one neighbor). In this case, multiple short van der Waals $C \cdots C$ contacts are formed between fullerenes in the 2.956–3.181 Å range (Fig. 2a, green dashed



Fig. 2 Packing of the Ni(dppp)· (η^2-C_{70}) units in **1**. View along the [010] direction on the fullerene layers (a) and along the [100] direction and fullerene layers (b). Green dashed lines show the shortest van der Waals $C \cdots C$ contacts between fullerenes. Solvent molecules are not depicted for clarity.

lines). The center-to-center distances with three other neighbors in the layer are essentially longer (10.66–12.30 Å) and prevent the formation of van der Waals $C \cdots C$ contacts between fullerenes (Fig. 2a). The C_{70} molecules have denser packing in the layers of **1** than that of the C_{60} molecules in the layers of **2**. This may be due to smaller size of vacancies occupied by solvent molecules. Fullerene layers are separated by bulky Ni(dppp) fragments (Fig. 2b).

The IR spectrum of 1 shows the absorption bands which can be attributed to ten C70 modes, Ni(dppp) and solvent molecules (see ESI†). It is known²² that the absorption band of C_{70} at 1430 \mbox{cm}^{-1} is sensitive to the charge state of C70 and shifts up to 1392-1394 cm⁻¹ for C_{70} . However, this band is not shifted in the spectrum of 1. Rather, C₇₀ and Ni(dppp) absorption bands coincide and show one intense band at 1431 cm⁻¹. Thus, no noticeable increase in electron density on C70 is observed in 1. On the contrary, two well separated bands at 1416 (C_{60}) and 1434 cm⁻¹ (Ni(dppp) were found in the spectrum of **2**. The shift of the $F_{1u}(4)$ mode of C_{60} (which is sensitive to the charge state of C_{60})^{27,28} from 1429 to 1416 cm⁻¹ indicates the increase in electron density on C_{60} .¹⁷ The coordination of Ni(dppp) to C_{70} splits the band at 576 cm^{-1} into two bands at 573 and 579 cm^{-1} due to C_{70} symmetry lowering. Similar splitting of the $F_{1\mu}(2) C_{60}$ mode at 576 cm⁻¹ into three bands at 573, 577 and 584 cm⁻¹ is observed in the spectrum of coordination complex 2.17

Starting C_{70} has a clear red color in *o*-dichlorobenzene. Upon coordination of Ni(dppp) to C_{70} the color of the solution turns red-brown. There are three bands in the UV-visible spectrum of Ni(dppp)·(η^2 - C_{70}) in *o*-dichlorobenzene: a weak band at 379 nm, an intense band at 467 nm and a broad weak band near 680 nm (Fig. 3a). Similar visible spectra are observed for coordination complexes of C_{70} with other metals. For example, Pd(dppf)·(η^2 - C_{70}) and Pt(dppf)·(η^2 - C_{70}) complexes (dppf is (diphenylphosphino)ferrocene) also manifest three bands in the visible spectrum with intense bands nearly at the same position (455 and 467 nm, respectively).¹³ We found that Ni(dppp)·(η^2 - C_{70}) is rather sensitive to oxygen. As a result of oxidation, the bands observed for the complex disappear and new bands attributed to starting C_{70} are manifested at 383 and 474 nm (Fig. 3b). The formation of



Fig. 3 UV-visible spectrum of (a) the Ni(dppp) $(\eta^2 - C_{70})$ coordination complex in *o*-dichlorobenzene solution measured in anaerobic conditions and (b) of the solution of the complex exposed in the air (b). For attribution of the bands see the text.

 C_{70} under oxidation of Ni(dppp)·(η^2 - C_{70}) indicates that oxygen can add to the Ni(dppp) fragment. The comparison of the Ni(dppp)·(η^2 - C_{70}) and the C_{70} spectra allows a conclusion that the C_{70} band at 383 nm nearly disappears upon the formation of the coordination complex, the band at 467 nm strongly increases in intensity (possibly due to the appearance of a new band at 467 nm or the increase in intensity and a slight shift of the C_{70} band at 474 nm), and a new broad band is manifested at 680 nm. Green Ni(dppp)·(η^2 - C_{60}) has two new bands in the visible spectrum at 436 and 672 nm.¹⁷ Therefore, the coordination of metals to both fullerenes C_{60} and C_{70} similarly changes their visible spectra. A new band appears or the absorption increases at 430–470 nm and weak broad bands are manifested at 670–680 nm.

Conclusion

In this work we developed a new reduction method to prepare nickel-fullerene coordination complexes from Ni(dppp)Cl₂, neutral fullerenes and sodium tetraphenylborate as a reductant. Single crystals of the first coordination complex of nickel with fullerene C₇₀, {Ni(dppp)· $(\eta^2$ -C₇₀)}·(C₆H₄Cl₂)_{0.5} (1), were synthesized allowing its crystal structure determination. It was shown that nickel forms unusually short Ni–C(C_{70}) bonds of 1.929(2) and 1.941(2) Å length. These bonds are slightly shorter than the Ni–C(C₆₀) bonds in Ni(dppp)·(η^2 -C₆₀) of 1.948–1.951(2) Å¹⁷ and are the shortest metal–carbon bonds among known $\eta^2\text{-}\text{complexes}$ of both fullerenes C₆₀ and C₇₀. The C-C bond to which Ni atom is coordinated elongates to 1.494(3) Å compared with the average length of these bonds in C₇₀ (1.381(2) Å) probably due to π -back donation. However, the IR band of C70 at 1430 cm⁻¹ which is sensitive to the charged state of C70 is not shifted in the spectrum of 1. The coordination of Ni(dppp) to C_{70} lowers its symmetry and splits the C_{70} band at 576 cm⁻¹ into two bands. The formation of Ni(dppp)·(η^2 -C₇₀) is accompanied by an increase in intensity of the band at 467 nm and the appearance of a new broad band at 680 nm. Similar changes were observed at the formation of Ni(dppp)·(η^2 -C₆₀) (two new bands appear at 436 and 672 nm).¹⁷ Ni(dppp)·(η^2 -C₇₀) is rather air sensitive in solution and is oxidized by air to starting C70.

Experimental

Materials

Ni(dppp)Cl₂ was purchased from Aldrich. C_{60} of 99.8% and C_{70} of 99% purity was received from MTR Ltd. Solvents were purified in an argon atmosphere. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH₂ under reduced pressure, benzene and hexane were distilled over Na/benzophenone. KBr pellets for IR and solutions of **1** and **2** for UV-visible spectra were prepared in a glove-box.

Synthesis

For preparation of complexes 1 and 2, a stoichiometric mixture of Ni(dppp)Cl₂ and fullerene was reduced by 2 equivalents of sodium tetraphenylborate in 10 ml of *o*-dichlorobenzene. The ratio of Ni(dppp)Cl₂: $C_{70}(C_{60})$: NaBPh₄ was 0.031:0.031:0.062 mmol for 1 and 0.042:0.042: 0.084 mmol for 2. All the components were dissolved at stirring for 5 h to yield clear red–brown (1) and deep-green (2) solutions which were filtered. The

crystals of {Ni(dppp)· (η^2-C_{70}) }·(C₆H₄Cl₂)_{0.5} (1) and {Ni(dppp)· (η^2-C_{60}) }·(Solvent) (2) were obtained by the diffusion of hexane layered over the *o*-dichlorobenzene solution during 1 month. The solvent was decanted from the crystals which were washed with hexane to yield black pikes (1) and small well-shaped black prisms (2). The crystals of 1 up to $0.2 \times 0.3 \times 0.5$ mm³ size were obtained in 50–60% yield.

The composition of **1** was determined from X-ray diffraction on a single crystal. Several crystals tested from the synthesis had the same unit cell parameters and were attributed to one crystal phase. The crystals of **2** were isostructural to those of the previously described complex {Ni(dppp)·(η^2 -C₆₀)}·(C₆H₁₄)_{0.84}·(C₆H₄Cl₂)_{0.16} (C₆H₁₄: hexane, C₆H₄Cl₂: *o*-dichlorobenzene).¹⁷

General

FT-IR spectra were measured in KBr pellets with a Perkin-Elmer 1000 Series spectrometer (400–7800 cm⁻¹). The visible spectrum in the range 400–900 nm was measured on a Specord M40.

X-Ray crystal structure determination

X-Ray diffraction data for 1 (see ESI[†]) were collected at 130(2) K on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated Mo-K α radiation using an Oxford Instrument Cryojet system. Raw data reduction on F^2 was carried out using CrysAlisPro, Oxford Diffraction Ltd. The structures were solved by the direct method²⁹ and refined by the full-matrix least-squares method against F^2 using SHELX-97.³⁰ Nonhydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H atoms were refined by the "riding" model with $U_{iso} = 1.2U_{eq}$ of the connected non-hydrogen atom or as ideal CH₃ groups with $U_{iso} = 1.5U_{eq}$.

Crystallographic data for 1. $C_{100}H_{28}CINiP_2$, $M_r = 1385.32$ g mol⁻¹, black, triclinic, space group $P\overline{1}$, a = 10.5609(6), b = 14.0596(7), c = 19.8880(10) Å, $\alpha = 100.191(4)$, $\beta = 97.361(4)$, $\gamma = 97.999(4)^{\circ}$, V = 2842.6(3) Å³, Z = 2, $D_c = 1.619$ g cm⁻³, F(000) = 1406, $\mu = 0.509$ mm⁻¹, T = 130(2) K, max. $2\theta = 62.52^{\circ}$, $R_{int} = 0.0386$, Reflections $I > 2\sigma(I) = 13129$, $R_1 = 0.0558$ [$I > 2\sigma(I)$], w $R_2 = 0.1530$, restraints/parameters 0/926, GOF = 1.036.

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