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Molecular Structure and Optical Properties of Nickel-bridged \( \{\text{Ni(Ph}_3\text{P)}\}_2(\mu_2-\eta^2, \eta^2-\text{C}_{60})_2 \) Dimer

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The compound containing fullerene dimers bonded through two nickel atoms \( \{\text{Ni(Ph}_3\text{P)}\}_2(\mu_2-\eta^2, \eta^2-\text{C}_{60})_2 \) 2C$_6$H$_2$Cl$_2$ (1) has been obtained as single crystals. Fullerenes are neutral in 1 showing zero-valent state of Ni. Nickel atoms are bonded with the \( \eta^2 \) coordination with Ni-C distances of 2.001(3)-2.037(3) Å and close approach of fullerenes with 9.716 Å center-to-center distance. The DFT calculations showed diamagnetic singlet ground state for this dimer.

Fullerene \( \text{C}_{60} \) contains two different types of C-C bonds. Shorter 6-6 bonds belonging to hexagon ring junction behave as olefinic units allowing the coordination of different transition metals to these bonds by the \( \eta^2 \)-type.\(^{1,5} \) Most of transition metal-fullerene complexes are monomeric but several metal bridged dimers are also known.\(^{6,8} \) For example, tungsten or molybdenum atoms\(^{9} \) or Ir$_2$ and Rh$_2$ clusters\(^{7,8} \) form such dimers. General methods for the preparation of metal-bridged fullerene dimers are absent. Nevertheless, the development of these methods is very important to obtain functional magnetic and conducting transition-metal fullerene complexes with dimeric or even polymeric structures.

We developed another approach to synthesize transition metal-fullerene complexes by the reduction of nickel(II) and cobalt(II) salts with diphosphine or phosphine ligands with \( \text{C}_{60} \).\(^{9,13} \) Reduction of Ni(L)$_2$X$_2$ (X = Cl and Br) and C$_6$H$_2$Cl$_2$ or C$_{70}$ yields monomeric \( \{\text{Ni(L)}(\eta^2-\text{C}_{60})\} \) and \( \{\text{Ni(dpdp)}(\eta^2-\text{C}_{70})\} \) complexes (L = dppe: 1,2-bis(diphenylphosphino)ethane; dpdp: 1,3-bis(diphenylphosphino)propane and dpff: 1,1’-bis(diphenylphosphino)ferrocene).\(^{9,11} \) Monomeric fullerene complexes with zero-valent cobalt atoms were obtained in the presence of benzonitrilite additionally coordinated to the cobalt atoms.\(^{12} \) However, when the mixture of Co(Ph$_3$P)$_2$Br$_2$ and C$_6$H$_2$Cl$_2$ is reduced, cobalt-bridged fullerene dimers form. These dimers contain closely located fullerene cages and paramagnetic Co$^0$ centers (S = 1/2). As a result, they show triplet state at room temperature and diamagnetic singlet ground state below 35 K.\(^{13} \) During the synthesis, one of two Ph$_3$P ligands coordinating to the cobalt atoms is substituted by fullerene. We suppose that when only one phosphine ligand is coordinated to the metal center, the tendency to form metal-bridged fullerene dimers facilitates to increase coordination number of metal atoms.

To check this hypothesis, we studied the reduction of NiI(CP(Ph$_3$P)Cl having one triphenylphosphine and one cyclopentadienyl ligands and C$_{60}$ by zinc dust in \( \sigma \)-dichlorobenzene at 160°C and stirring of the obtained solution at 100°C during 4 hours. Pale green solution characteristic of transition metal-fullerene complexes is formed, from which small black crystals were obtained by slow diffusion of \( n \)-hexane, and which composition is \( \{\text{Ni(Ph}_3\text{P)}\}_2(\mu_2-\eta^2, \eta^2-\text{C}_{60})_2 \) 2C$_6$H$_2$Cl$_2$ (1). A new type of nickel-bridged fullerene dimers was found. In contrast to previously studied \( \{\text{Co(Ph}_3\text{P})(\text{C}_6\text{H}_5\text{CN})\}_2(\mu_2-\eta^2, \eta^2-\text{C}_{60})_2 \) dimers (2),\(^{13} \) two zero-valent nickel atoms coordinate in 1 by \( \eta^2 \)-type to two 6-6 fullerene bonds belonging to one hexagon of C$_{60}$ providing close Ni…Ni and interfullerene distances. We present molecular structure and optical properties of these dimers. DFT calculations based on X-ray diffraction data allow one to elucidate electronic structure of these dimers.

The IR-spectrum of 1 showed bands of C$_{60}$, Ph$_3$P and C$_6$H$_2$Cl$_2$ (Table S1). IR-active bands of C$_{60}$, Ph$_3$P, and C$_6$H$_2$Cl$_2$ (4) mode from 1429 to 1396-1388 cm$^{-1}$.

The IR-spectrum of 1 shows bands of C$_{60}$, Ph$_3$P and C$_6$H$_2$Cl$_2$ (Table S1). IR-active bands of C$_{60}$ were observed at 525, 578, 1183 and 1420 cm$^{-1}$. The last band appears only as a shoulder of more intense band of Ph$_3$P at 1433 cm$^{-1}$. Transition of C$_{60}$ from neutral to radical anion state is accompanied by the shift of \( F_{1s}(4) \) mode from 1429 to 1396-1388 cm$^{-1}$.\(^{14,15} \) The shift of this mode to 1420 cm$^{-1}$ in the spectrum of 1 can be due to the \( \pi \)-back-donation.\(^9 \)

The UV-visible-NIR spectrum of 1 is shown in Figure S1. It shows a band of C$_{60}$ at 338 nm and two weak bands in the visible range at 625 and 709 nm which can be attributed to charge transfer transition in the dimers (for the assignment of these bands, see the section about DFT calculations). The lack of the C$_{60}$“bands at 950 and 1070 nm\(^{14,15} \) indicates neutral state of fullerenes in the dimers. Thus, nickel atoms should have zero-valent state and correspondingly \( d^{10} \) electron configuration. The absence of charge transfer from Ni$^{10+}$ to fullerene was found in other monomeric Ni(L)-C$_{60}$ complexes.\(^9\)

The crystal structure analysis\(^16 \) revealed that the \( \{\text{Ni(Ph}_3\text{P)}\}_2(\text{C}_{60})_2 \) dimer is situated on a mirror plane. The Ni(Ph$_3$P) fragment is disordered between two positions having 0.936(0.964) occupancies (see Supporting Information for more details). In the major component each nickel atom is linked to two fullerene cages by the \( \eta^2 \)-type with slightly
asymmetric Ni-C bonds of 2.001-2.006(3) and 2.014-2.037(3) Å length (Figs. 1 and 2). These bonds are slightly shorter than the Co-C bonds in the dimer 2. Coordination in 1 is realized to the 6-6 bonds of C$_{60}$ elongated to 1.447-1.449(4) Å in comparison with the average length of the other 6-6 bonds in C$_{60}$ (1.390(4) Å). Moreover, we found that all 6-5 and 6-6 C-C bonds of C$_{60}$ with carbon atoms involved in the coordination are elongated by 0.05-0.07 Å (Fig. 2). The strongest elongation is observed for the 6-5 bond located between two carbon atoms involved in the coordination (1.501-1.506(5) Å vs average value of 1.434(4) Å for the other 6-5 bonds in C$_{60}$). This elongation can be due to metal-to-C$_{60}$ π-back-donation. Two nickel atoms coordinate to two 6-6 bonds belonging to one hexagon. Such type of coordination of metal atoms is different from that in dimer 2 in which 2-6-6 bonds involved in coordination with cobalt are separated by one pentagon. As a result, two nickel atoms approach essentially closer to each other in 1 with the Ni--Ni distance of only 3.4422(6) Å. This is shorter than the sum of van der Waals (vdW) radii of two nickel atoms. Cobalt atoms are essentially separated farther in 2 by 5.308(3) Å. Two fullerene cages approach very close to each other in 1 with a center-to-center interfullerene distance of 9.716 Å and two very short intercage C...C contacts of 2.679(4) Å. Among metal-bridged dimers only dimer 2 has close interfullerene distances and C...C contacts of 9.696 and 2.815(2) Å. In the other metal-fullerene dimers, these parameters are: 10.29 and 3.25 Å for Ir$_4$(CO)$_8$(μ$_4$-CH)(PM$_2$)$_2$(PMe$_2$)(CNR)(μ-η$_6^2$-C$_{60}$)(μ-η$_6^2$-η$_6^2$-C$_{60}$), 7 10.34 and 3.59 Å for Rh$_8$(CO)$_4$(dpmm)$_2$(μ-η$_6^2$-η$_6^2$-η$_6^2$-C$_{60}$), and 11.58 and 4.39 Å for [M(Bη$_6^2$-C$_{60}$)$_2$(CO)$_4$(dbcbipy)] [M = W and Mo, dbcbipy = 4,4′-di(butyl carboxyl)-2,2′-bipyridine].

Additionally to two fullerenes, one triphenylphosphine ligand is coordinated to each nickel atom with Ni-P bond length of 2.226(1) Å. As a result, a nickel atom is surrounded by four carbon and one phosphorus atoms forming distorted pentagonal environment (Fig. 2). Four carbon atoms form the C$_4$ plane and nickel atoms are only slightly displaced out of this plane by 0.164 Å.

The {Ni(Ph$_3$P)$_2$C$_{60}$} dimers form zigzag chains in the ac plane. The center-to-center distances between two fullerenes from the neighboring dimers are 10.041 Å and several short interfullerene C...C contacts are formed in the 3.31-3.40 Å range (Fig. S4).

The EPR spectrum of 1 measured in anaerobic conditions showed that 1 is EPR silent and diamagnetic. The absence of charge transfer from Ni$^0$ to fullerene is in accordance with optical spectra of 1. No charge transfer was found previously for a series of monomeric fullerene complexes: {Ni(L)(η$_5^2$-C$_{60}$)} (L = dppe, dppp, dpf)$_{10}$. In the absence of charge transfer to fullerene, nickel atoms should have diamagnetic d$^8$ electron configuration and also be EPR silent. We also found that 1 is oxidized in solid state and broad Lorentzian signal is appeared. (g = 1.879 and linewidth (ΔH) of about 64 mT at room temperature). This signal can appear due to decomposition of the nickel-fullerene complex and oxidation of Ni$^0$ to Ni$^1$. Generally, Ni$^1$ complexes show broad isotropic EPR signals with g-factors of 2.000-2.080 and ΔH of about 26 mT.

Theoretical analysis based on density functional theory (DFT) was performed using the crystal structure of the [Ni(Ph$_3$P)$_2$C$_{60}$] dimer with C$_2$ symmetry (Figs. 1a and S5). The singlet and triplet states were investigated at the B3LYP, CAM-B3LYP, and oB97X-D/LanL2DZ/6-31G(d,p) levels of theory. The calculated results were qualitatively similar for three functionals. The total and relative energies, and <$S^z$> values are shown in Table S2, and the energy diagrams of frontier orbitals for the singlet states are shown in Fig. 3, S6, and S7. Judging from the <$S^z$> values, the spin contamination is nearly negligible for the calculated triplet states since the <$S^z$> values for the pure triplet state is equal to 2. All three functionals indicate that the closed-shell singlet states are much more stable than the corresponding triplet states, which must

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**Fig. 1.** Molecular structure of {Ni(Ph$_3$P)$_2$C$_{60}$} dimers in 1 in major orientation viewed along (a) and perpendicular (b) to the Ni--Ni line. Carbon atoms are indicated in brown, nickel atoms are green, and phosphorus atoms are orange. Solvent molecules are not shown. Ellipsoids are shown with 50% probability.

**Fig. 2.** Bond lengths in the fragment in which two nickel atoms coordinate to two hexagons of C$_{60}$ molecules.
be thermally inaccessible since the calculated gap more than 1.64 eV. The theoretical analysis supports the diamagnetic feature of \{Ni(PhP)\}_2(C_60)\_2 by magnetic measurements. The highest occupied molecular orbital (HOMO) located around nickel atoms is antibonding between the nickel and C\_60 molecules but bonding between nickel and Ph\_2P molecules, whereas the lowest unoccupied molecular orbital (LUMO) and (LU+1)MO are mainly localized on C\_60 molecules, respectively (Fig. 3). By natural population analysis, charges of Ni, C\_60 and Ph\_2P were estimated to be about +0.22–−0.23, −0.54–−0.58, and +0.33–+0.34, respectively.

To gain further insight on the UV-vis-NIR spectrum of 1, time-dependent DFT (TD-DFT) analysis was carried at the TDDC3LYP/LanL2DZ/6-31G(d,p) level of theory. The excitation properties of low-lying excited states (S\_0 → S\_1) molecules is characterized mainly as HO and (HO-2)MOs excitation, and the second lowest S\_0 → S\_2 transition is as HO → LU+1, and (HO-2) → LUMO excitations. Comparing charge distributions at the S\_1 and S\_2 states to that of the S\_0 state, the S\_0 → S\_1 (S\_2) transition is described as a charge transfer transition from nickel, Ph\_2P, and C\_60 (C\_60) (C\_60) molecules to C\_60 (C\_60) molecules. However, the degree of charge transfer is small.

Conclusions

Thus, the first nickel-bridged fullerene dimer was obtained in which two C\_60 cages are bonded through two nickel atoms \{Ni(PhP)\}_2(\mu_2-n, n^2-C_60\}_2. The structure of the present dimer is distinguished from the structures of the other known metal-bridged fullerene dimers not only due to short distances between fullerene cages but also short Ni...Ni distance. The presented synthetic approach, in which the reduction of divalent metal coordinated with one phosphine and another type of ligand to increase the coordination number, opens the way to obtaining dimeric transition metal complexes with fullerences. We suppose that even polymeric metal-fullerene complexes can be obtained by this method. The Ni\^ 2\textsuperscript{+} atoms used in the synthesis are diamagnetic due to the d\textsuperscript{10} electron configuration. However, we expect that the preparation of such dimers with paramagnetic zero-valent cobalt atoms or some other paramagnetic metals can provide compounds with promising magnetic properties. This work is now in progress.

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Nickel-bridged fullerene dimer, \( \{\text{Ni(Ph,P)}\}_2(\mu_2,\eta^2,\eta^2-C_{60})_2 \), was obtained and studied by X-ray crystallography. Two \( C_{60} \) cages are \( \eta^2 \)-bonded through two nickel atoms separated only by 3.442(3) Å distance (see picture: Ni green, P orange, C brown). Optical and EPR spectra indicate no charge transfer from Ni to \( C_{60} \) and zero-valent state of \( \text{Ni}^{0} \) with diamagnetic \( d^{10} \) electron configuration.