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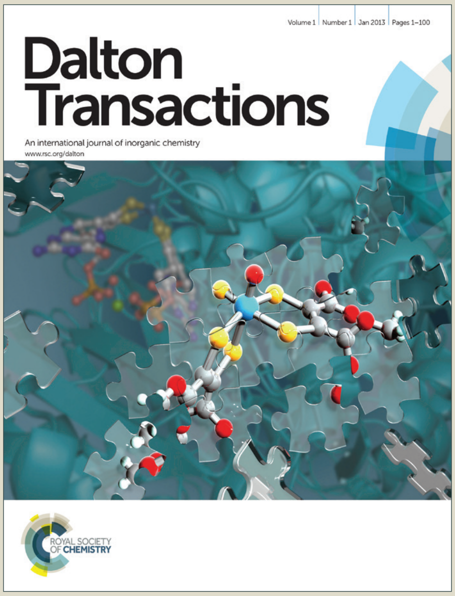

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Molecular Structure and Optical Properties of Nickel-bridged $\{Ni(Ph_3P)\}_2(\mu_2-\eta^2, \eta^2-C_{60})_2$ Dimer

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The compound containing fullerene dimers bonded through two nickel atoms $\{Ni(Ph_3P)\}_2(\mu_2-\eta^2,\eta^2-C_{60})_2\cdot 2C_6H_4Cl_2$ (1) has been obtained as single crystals. Fullerenes are neutral in 1 showing zero-valent state of Ni. Nickel atoms are bonded with the η^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 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 η^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[6] or Ir_4 and Rh_6 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 C_{60}.[9-13] Reduction of $Ni(L)X_2$ (X = Cl and Br) and C_{60} or C_{70} yields monomeric $\{Ni(L)(\eta^2-C_{60})\}$ and $\{Ni(dppp)(\eta^2-C_{70})\}$ complexes (L = dppe: 1,2-bis(diphenylphosphino)ethane; dppp: 1,3-bis(diphenylphosphino)propane and dppf: 1,1′-bis(diphenylphosphino)ferrocene).[9-11] Monomeric fullerene complexes with zero-valent cobalt atoms were obtained in the presence of benzonitrile additionally coordinated to the cobalt atoms.[12] However, when the mixture of $Co(Ph_3P)_2Br_2$ and C_{60} 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_3P 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 $Ni^{II}Cp(Ph_3P)Cl$ having one triphenylphosphine and one cyclopentadienyl ligands and C_{60} by zinc dust in *o*-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 was $\{Ni(Ph_3P)\}_2(\mu_2-\eta^2,\eta^2-C_{60})_2\cdot 2C_6H_4Cl_2$ (**1**). A new type of nickel-bridged fullerene dimers was found. In contrast to previously studied $\{Co(Ph_3P)(C_6H_5CN)\}_2(\mu_2-\eta^2,\eta^2-C_{60})$ dimers (**2**),[13] two zero-valent nickel atoms coordinate in **1** by η^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_3P and $C_6H_4Cl_2$ (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_3P at 1433 cm^{-1}. Transition of C_{60} from neutral to radical anion state is accompanied by the shift of $F_{1u}(4)$ 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 π-back-donation.[1]

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 $C_{60}^{\bullet-}$ 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^0 to fullerene was found in other monomeric Ni(L)-C_{60} complexes.[9,10]

The crystal structure analysis[16] revealed that the $\{Ni(PPh_3)\}_2(C_{60})_2$ dimer is situated on a mirror plane. The $Ni(Ph_3P)$ fragment is disordered between two positions having 0.936/0.064(2) occupancies (see Supporting Information for more details). In the major component each nickel atom is linked to two fullerene cages by the η^2-type with slightly

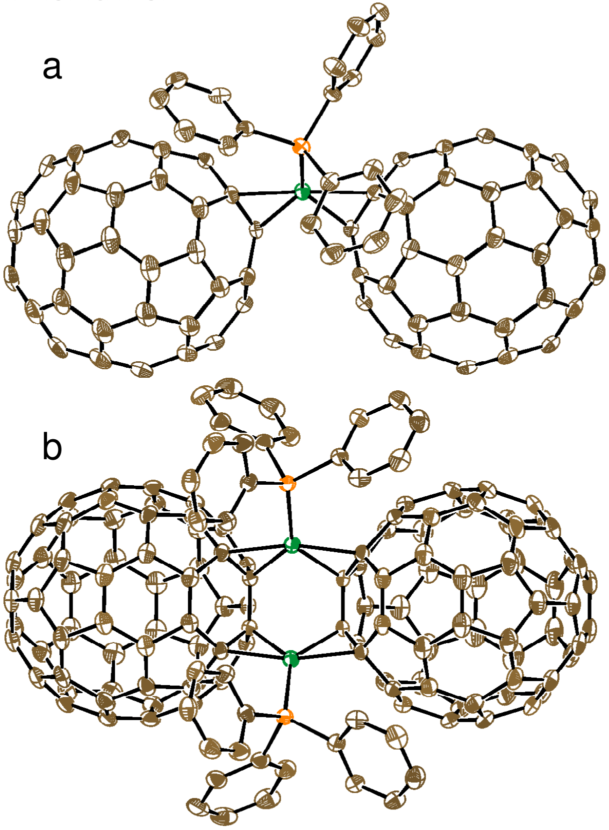

Fig. 1. Molecular structure of $\{Ni(Ph_3P)\}_2(C_{60})_2$ dimers in **1** in major orientation viewed along (a) and perpendicular (b) to the Ni···Ni line. Carbon atoms are indicated in brown, nickel atoms are green, and phosphorus atoms are orange. Solvent molecules are not shown. Ellipsoids are shown with 50% probability.

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**[13]. 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.[1] 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 two 6-6 bonds involved in coordination with cobalt are separated by one pentagon.[13] 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.[13] 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.[13] In the other metal-fullerene dimers, these parameters are: 10.29 and 3.25 Å for $Ir_4(CO)_3(\mu_4\text{-}CH)(PMe_3)_2(PMe_2)(CNR)(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_{60})$,[7] 10.34 and 3.59 Å for $Rh_6(CO)_9(dppm)_2(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[8] and 11.58 and 4.39 Å for $[M(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]$ [M = W and Mo, dbcbipy = 4,4′-di(butyl carboxyl)-2,2′-bipyridine][6].

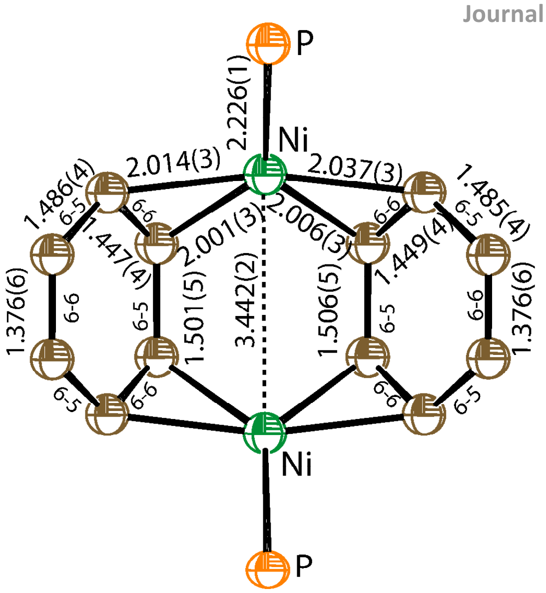

Fig. 2. Bond lengths in the fragment in which two nickel atoms coordinate to two hexagons of C_{60} molecules.

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 $\{Ni(Ph_3P)\}_2(C_{60})_2$ 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: $\{Ni(L)(\eta^2\text{-}C_{60})\}$ (L = dppe, dppp, dppf)[9, 10]. In the absence of charge transfer to fullerene, nickel atoms should have diamagnetic d^{10} 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^I. Generally, Ni^I complexes show broad isotropic EPR signals with g-factors of 2.000-2.080 and ΔH of about 26 mT.[17]

Theoretical analysis based on density functional theory (DFT) was performed using the crystal structure of the $\{Ni(Ph_3P)\}_2(C_{60})_2$ dimer with C_S symmetry (Figs. 1a and S5).[18] The singlet and triplet states were investigated at the B3LYP, CAM-B3LYP, and ωB97X-D/LanL2DZ/6-31G(d,p) levels of theory. The calculated results were qualitatively similar for three functionals. The total and relative energies, and $<S^2>$ 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 $<S^2>$ values, the spin contamination is nearly negligible for the calculated triplet states since the $<S^2>$ 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

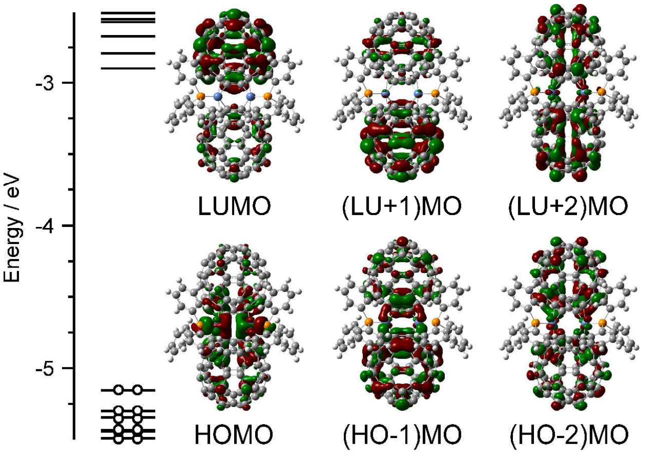

Fig. 3. Energy diagram of frontier orbitals for the ${}^1A'$ state of $\{Ni(Ph_3P)\}_2(C_{60})_2$ calculated at the RB3LYP/LanL2DZ/6-31G(d,p) level of theory.

be thermally inaccessible since the calculated gap more than 1.64 eV. The theoretical analysis supports the diamagnetic feature of $\{Ni(Ph_3P)\}_2(C_{60})_2$ 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_3P molecules, whereas the lowest unoccupied molecular orbital (LUMO) and (LU+1)MO are mainly localized on C_{60}(B) and C_{60}(A) molecules, respectively (Fig. 3). By natural population analysis, charges of Ni, C_{60}, and Ph_3P 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 TD-RCAM-B3LYP/LanL2DZ/6-31G(d,p) level of theory. The excitation properties of low-lying excited states (S_n, n = 1-6) along with the ground state (S_0) are summarized in Table S4. The lowest $S_0 \rightarrow S_1$ transition is characterized mainly as HO and (HO−2)MOs →LUMO excitations, and the second lowest $S_0 \rightarrow S_2$ 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 $S_0 \rightarrow S_1$ (S_2) transition is described as a charge transfer transition from nickel, Ph_3P, and C_{60}(A) (C_{60}(B)) molecules to C_{60}(B) (C_{60}(A)) 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 $\{Ni(Ph_3P)\}_2(\mu_2\text{-}\eta^2,\eta^2\text{-}C_{60})_2$. 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 fullerenes. We suppose that even polymeric metal-fullerene complexes can be obtained by this method. The Ni^0 atoms used in the synthesis are diamagnetic due to the d^{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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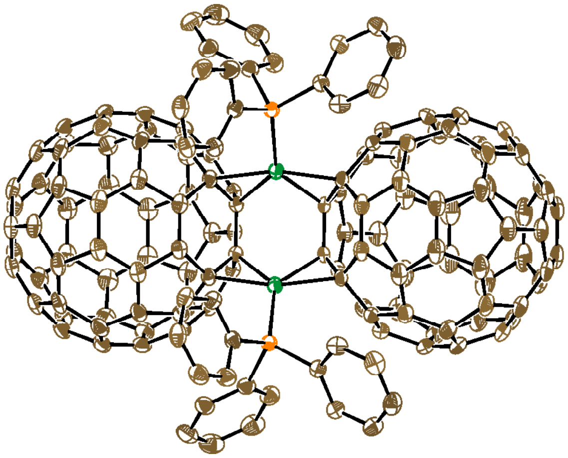
Electronic Supplementary Information (ESI) available: a CIF file of **1**, synthesis and characterization data of **1**, including IR, UV−visible−NIR, and details of the calculations. See DOI: 10.1039/c000000x/

1 P. J. Fagan, J. C. Calabrese and B. Malone, *Acc. Chem. Res.* 1992, **25**, 134.
2 V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, S. V. Lindeman, I. A. Guzey and Yu. T. Struchkov, *Organometallics*, 1993, **12**, 991.
3 A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead and S. R. Parkin, *J. Am. Chem. Soc*. 1991, **113**, 8953.
4 P. J. Fagan, J. C. Calabrese and B. Malone, *J. Am. Chem. Soc*. 1991, **113**, 9408.
5 A. L. Balch and M. M. Olmstead, *Chem. Rev*. 1998, **98**, 2123.
6 X. Jin, X. Xie, K. Tang, *Chem. Commun*. 2002, 750.
7 G. Lee, Y. -J. Cho, B. K. Park, K. Lee and J. T. Park, *J. Am. Chem. Soc*. 2003, **125**, 13920.
8 K. Lee, H. Song, B. Kim, J. T. Park, S. Park and M. -G. Choi, *J. Am. Chem. Soc*. 2002, **124**, 2872.
9 D. V. Konarev, S. S. Khasanov, E. I. Yudanova, and R. N. Lyubovskaya, *Eur. J. Inorg. Chem.* 2011, 816.
10 D. V. Konarev, S. I. Troyanov, S. S. Khasanov and R. N. Lyubovskaya, *J. Coord. Chem*. 2013, **66**, 4178.
11 D. V. Konarev, S. V. Simonov, S. S. Khasanov, R. N. Lyubovskaya, *Dalton Trans* 2011, **40**, 9176.
12 D. V. Konarev, S. S. Khasanov, S. I. Troyanov, Y. Nakano, K. A. Ustimenko, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Inorg. Chem*. 2013, **52**, 13934.
13 D. V. Konarev, S. I. Troyanov, Y. Nakano, K. A. Ustimenko, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Organometallics*, 2013, **32**, 4038.
14 C. A. Reed and R. D. Bolskar, *Chem. Rev*. 2000, **100**, 1075.
15 D. V. Konarev and R. N. Lyubovskaya, *Russ. Chem. Rev*. 2012, **81**, 336.
16 Crystal data for **1**: $C_{168}H_{38}Cl_4Ni_2P_2$, M_r = 2377.14, orthorhombic, *P*nma, a = 25.817(1), b = 22.976(1), c = 15.7552(8) Å, V = 9345.5(7) $Å^3$, Z = 4, 134691 reflections collected, 11051 independent; R_1 = 0.0591 for 10335 observed data [$I > 2\sigma(F)$] with 18 restraints and 878 parameters; wR_2 = 0.1384 (all data); final GOF = 1.016. CCDC 999053.
17 V. R. Flid, O. S. Manulik, L. M. Grundel and A.P. Belov, *Teoret. Experim. Khim.* 1990, **26**, 490.
18 Gaussian 09, Revision D.01

SYNOPSIS TOC



Nickel-bridged fullerene dimer, $\{Ni(Ph_3P)\}_2(\mu_2\text{-}\eta^2,\eta^2\text{-}C_{60})_2$, was obtained and studied by X-ray crystallography. Two C_{60} cages are η^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 Ni^0 with diamagnetic d^{10} electron configuration.