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Theoretical study of N_2 coordination in metal complexes with fullerene ligands

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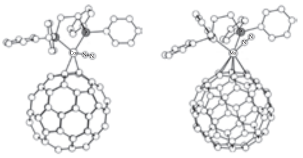
Quantum chemical modeling demonstrates the stability of Co^0 and Mo^0 metal complexes with N_2 and C_{60} ligands in the coordination sphere. These complexes may be used as convenient synthons for the synthesis of polynuclear metal complexes with bridging fullerene ligands.



In metal complexes, C_{60} usually acts as a neutral electron-acceptor ligand. This favors the inside stabilization of metal complexes in a zero-valent state. The Co^0 complex $Co(\eta^2\text{-}C_{60})(dppe)(PhCN)$ **1** containing a coordinated benzonitrile molecule along with a fullerene ligand and 1,2-bis(diphenylphosphino)ethane (dppe) was recently obtained.[1] Since the PhCN ligand can be considered as an analogue of N_2, we can point out an analogy of this complex with various nitrogen Co phosphine complexes, in which the metal atom has an oxidation state of 1,[2] 0,[3] or –1,[4] obtained in a similar way by the reduction of cobalt chloride complexes under nitrogen. Thus, it can be assumed that the Co complex containing both C_{60} and N_2 ligands can be prepared analogously to **1**, but under a nitrogen atmosphere in the absence of PhCN. Note that the mixed complexes of Mo, $Mo(C_{60})(dppe)(CO)_3$ incorporating C_{60} and the CO molecule isoelectronic to N_2 are known.[5]

Typically, nitrogen complexes are not very stable, and a coordination vacancy formed can be filled with a more strongly bound ligand such as CO.[6] In complex **1**, benzonitrile acts as a blocking ligand because upon the reduction of $Co(dppe)Br_2$ in the absence of PhCN in the coordination sphere of the Co atom the second C–C bond of another fullerene molecule appears.[7] Therefore, mixed fullerene–nitrogen complexes are interesting as convenient synthons for the controlled production of various complexes with bridging fullerene ligands, including heterometallic ones. Currently such complexes are known, in which a zero-valent metal atom with a phosphine ligand coordinates two fullerene ligands.[7–10] As a result, binuclear or polynuclear complexes (polymer chains) are formed in which the C_{60} molecule serves as a bridging ligand. However, they are formed by a multistep process of reduction of metal halide complexes.

Quantum-chemical modeling was used to reveal the possibility of the existence of fullerene–nitrogen complexes and their stability. For this purpose, we used the PBE density functional[11] and full-electron Λ2 basis[12] {Co: (23*s*,18*p*,13*d*,8*f*,4*g*)/[8*s*,7*p*,5*d*,3*f*,1*g*], P: (18*s*,13*p*,5*d*,2*f*)/[5*s*,4*p*,2*d*,1*f*], N, C: (12*s*,8*p*,4*d*,2*f*)/[4*s*,3*p*,2*d*,1*f*], H: (8*s*,4*p*,2*d*)/[3*s*,2*p*,1*d*]} of cc-pVTZ quality. Note that the results for the Co systems do not differ much from those of calculation using TZV2p triple-zeta basis set[13] for valence shells and SBK-JC relativistic pseudo-potentials[14] for the core electrons. This approach was successively used in a study of the structure and reactivity of transition metal complexes of fullerene.[15] For the Mo atoms, some relativistic effects start appearing, so for calculation of Mo complexes it is better to use the pseudopotential method. All calculations were performed using the PRIRODA[13] software package and the computing facilities of Joint Supercomputer Center of the Russian Academy of Sciences.

The calculated structure of **1** is consistent with experimental data [Figure 1(*a*)]. Test calculations of nitrogen complexes $CoH(PPh_3)_3N_2$ **2** and $\{Co[(Ph_2PCH_2)_3CMe]\}_2(\mu\text{-}N_2)$ **3** also give results close to the experimental data. The crystal structure has two chemically equivalent complexes **2**, in which the Co–N and N–N distances are 1.784(13), 1.829(12) and 1.101(12), 1.123(13) Å, respectively.[2] The calculated values of these distances are 1.785 and 1.133 Å, respectively. Experimental (2088 cm^{-1}) and theoretical (2064 cm^{-1}) N–N vibration frequencies in this complex are also consistent. For complex **3**, Co–N and N–N distances are 1.774 and 1.172 Å, and the experimental values[3] are 1.761 and 1.178 Å, respectively. In this complex, symmetrical stretching N–N

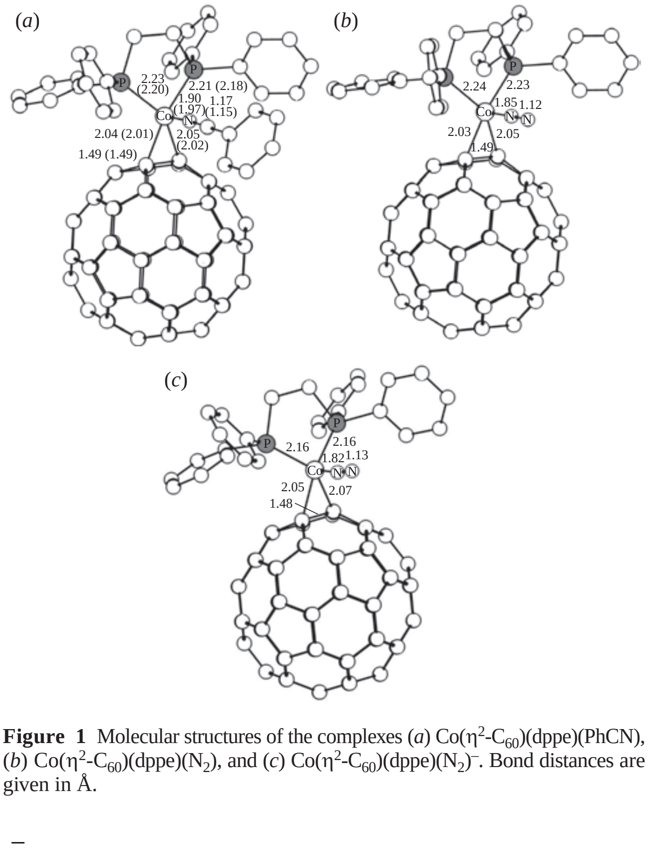


Figure 1 Molecular structures of the complexes (*a*) $Co(\eta^2\text{-}C_{60})(dppe)(PhCN)$, (*b*) $Co(\eta^2\text{-}C_{60})(dppe)(N_2)$, and (*c*) $Co(\eta^2\text{-}C_{60})(dppe)(N_2)^-$. Bond distances are given in Å.

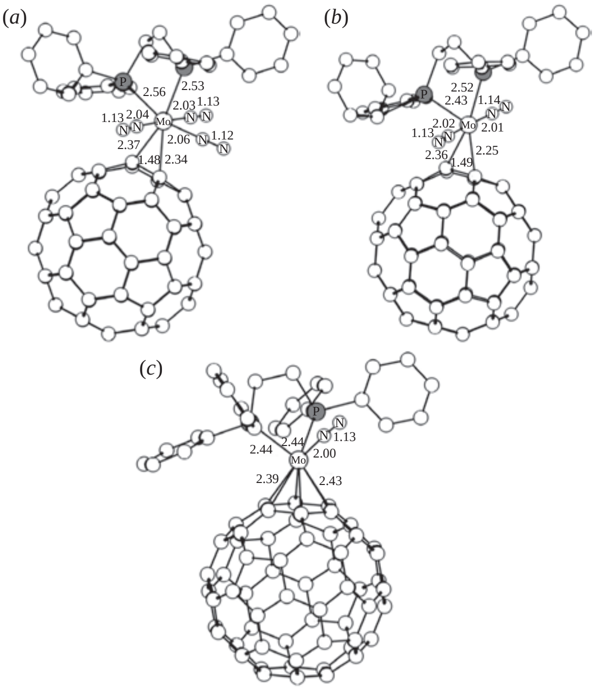


Figure 2 Molecular structures of the complexes (*a*) Mo(η^2-C_{60})(dppe)$(N_2)_3$, (*b*) Mo(η^2-C_{60})(dppe)$(N_2)_2$, and (*c*) Mo(η^6-C_{60})(dppe)(N_2). Bond distances are given in Å.

vibrations are not active in the IR spectrum and their frequency is unknown. For the simplest complexes of Co^0, formed by the interaction of Co atoms and nitrogen molecules in a low-temperature matrix for linear (ground state) and side-on coordination of N_2, vibration frequencies 1874 and 2101 cm^{-1}, respectively, are observed.[16] The calculated values are 1847 and 2102 cm^{-1}.

Replacing PhCN with N_2 in **1** has a little effect on the structural characteristics of the complexes [Figures 1(*a*),(*b*)] and on the distribution of charge and spin density (Table 1). PhCN binding energy (19.1 kcal mol^{-1}) and that of N_2 (14.0 kcal mol^{-1}) are also close. Small elongation of N–N bond in the complex by 0.025 Å corresponds to the lowering of N–N stretching vibration frequency up to 2146 cm^{-1}. From the found values of standard enthalpy (–15.0 kcal mol^{-1}) and entropy (–41.7 cal mol^{-1} K^{-1}) for N_2 binding, the dissociation constant at 360 K in a gas phase can be estimated as 1 at 360 K. In the anionic complexes [Figure 1(*c*), Table 1], only a small portion of the negative charge is localized on the Co atoms. Therefore, the N_2 molecule binding energy slightly increases to 15.0 kcal mol^{-1}.

The Mo nitrogen complexes are widely known.[18] Measured enthalpy of N_2 binding in the Mo^{II} complex Cp*MoCl$(PMe_3)_2(N_2)$ has a relatively large value of –22.8 kcal mol^{-1}.[19] We believe that the mixed fullerene–nitrogen Mo complexes can be prepared using a different strategy, *i.e.* by the reduction of suitable nitrogen complexes in the presence of C_{60}.

Table 1 Charges and spin densities (in parentheses) on the selected atoms and atomic fragments.[a]

Atomic fragment	Complex		
	$CoC_{60}(dppe)(PhCN)$	$CoC_{60}(dppe)(N_2)$	$CoC_{60}(dppe)(N_2)^-$
Co	–0.128 (0.992)	–0.132 (0.978)	–0.215 (0)
PhCN or N_2	0.112 (0.010)	0.005 (0.009)	–0.186 (0)
dppe	0.423 (0.048)	0.473 (0.050)	0.091 (0)
C_{60}	–0.407 (–0.049)	–0.345 (–0.037)	–0.780 (0)
C_2 fragment bound to the Co atom	–0.091 (–0.019)	–0.094 (–0.018)	–0.088 (0)

[a] Charges and spin densities are calculated according to Hirshfeld.[17]

To investigate the stability of fullerene–nitrogen–Mo complexes, a replacement of the CO ligand with the N_2 one in complex Mo(η^2-C_{60})(dppe)$(CO)_3$ **4** was considered.[4] For **4**, the calculated bond lengths are Mo–C_{cis}(O) 2.040 (2.033) Å, Mo–C(O) 2.008 (2.010) Å, C–O 1.164 (1.148) Å, Mo–C 2.366 (2.308) Å, Mo–P 2.600 (2.545) and 2.521 (2.475) Å, and they are consistent with the experimental data[5] given in parentheses. The structure of the complex obtained by replacing CO with N_2 is shown in Figure 2(*a*). Removing all of N_2 molecules requires an energy of 55.0 kcal mol^{-1}; however, the binding energy of the N_2 ligands is very unevenly distributed, and more than one third, 20.2 kcal mol^{-1}, falls on the first molecule N_2. A twice less energy of 11.0 kcal mol^{-1} is required to remove the second N_2 molecule. The corresponding standard Gibbs free energies increased under removal of the first, second and third N_2 molecules by 8.9, 0.4 and 13.2 kcal mol^{-1}, respectively. The reason for that large difference is another coordination motive of fullerene molecules in the starting Mo(η^2-C_{60})(dppe)$(N_2)_2$ [Figure 2(*b*)] and the final Mo(η^6-C_{60})(dppe)(N_2) [Figure 2(*c*)] complexes. The instability of the complex with one N_2 ligand relative to η^2–η^5 shift is caused by the tendency of Mo atoms to have high coordination numbers. Thus, under the conditions of thermal dissociation of Mo(η^2-C_{60})(dppe)$(N_2)_3$, we should expect the formation of an intermediate complex with one nitrogen ligand and η^6-coordinated fullerene. The η^5-C_{60} complexes are known only in the presence of substituents surrounding a C_5 ring,[20] although the pattern of C_{60} coordination through five-membered and six-membered carbon rings is being intensively studied theoretically.

In conclusion, a quantum chemical modeling demonstrates the stability of metal complexes of Co^0 and Mo^0 with N_2 and C_{60} ligands. These complexes may be used as convenient synthons for polynuclear metal complexes with bridging fullerene ligands.

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