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Synthesis, X-ray crystal structure and quantum-chemical study of new dinuclear cobalt complex $\{Co_2[\mu\text{-}O_2P(H)Mes]_2(bpy)_4\}Br_2$

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All reactions and manipulations were carried out under dry, pure nitrogen using standard Schlenk apparatus. THF and n-hexane were distilled from sodium/benzophenone and stored under nitrogen before use. CCl_4 and ethanol were purified by distillation. DMF was dried by stirring with calcium hydride (10g/l) for 2 h and then distilled at low pressure. After purification all solvents were stored under an atmosphere of dry nitrogen. 2,2'-bipyridine (Alfa Aesar), $CoBr_2$ x $6H_2O$ (Fluka) are commercially available and were used without additional purification. MesP(O)(OH)H was prepared according to described procedure.[1,2]

IR spectra were recorded on a FTIR spectrometer Bruker Vector-22 in the 400 – 4000 cm^{-1} range at an optical resolution of 4 cm^{-1}. Solid samples were prepared as KBr pellets. FT Raman spectra were recorded on a Bruker RAM II module (using a Ge detector) attached to a Bruker Vertex 70 FTIR spectrometer in the 4000–10 cm^{-1} range at an optical resolution of 4 cm^{-1}. The Nd:YAG laser with a wavelength of 1064 nm (power of 100 mW) was used as a source of excitation. The samples were placed in a standard cylindrical aluminum sample pan. Elemental analysis was performed on a EuroVector CHNS-O Elemental Analyser EA3000. The cobalt and phosphorus contents of the obtained compounds were determined by inductively coupled plasma mass spectrometry (ICP-MS) on a Perkin-Elmer Elan DRC II mass spectrometer (USA) and atomic absorption spectroscopy (AAS) on a Carl Zeiss AAS1 spectrometer.

X-ray diffraction analysis was performed on automatic diffractometer "Bruker Smart APEX II CCD (λMoK_α). The structure was solved by direct method using SIR program and refined by the full matrix least-squares using SHELXL-97 program.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed into the geometrically calculated positions and refined as riding atoms. All calculations were performed using WinGX program.[4] All the figures and analysis of intermolecular interactions were performed using PLATON program.[5]

All quantum-chemical computations reported in this study were carried out using the Gaussian 09[6] suite of programs. Calculations were performed with Becke's three parameter hybrid exchange functional[7] and the gradient-corrected nonlocal correlation functional of Lee, Yang and Parr[8] (B3LYP). The ligand atoms H, C, O and P were treated with 6-31G* basis set,[9] while for Co atoms ECP LanL2DZ basis set[10] was used. This method was shown to produce good results when describing structural and spectroscopic parameters of various organic compounds and their complexes.[11] Stationary points were characterized as minima by analysis of the Hessian matrices. For modeling the case of antiparallel electron spins on metal centers broken symmetry approach[12,13] was applied. The experimental and calculated selected bond lengths and angles for complex **1** are mentioned in Table S1.

Table S1 Comparison of experimental and calculated selected bond lengths (Å) and angles (°) for complex **1**.

	X-Ray	B3LYP
Co(1)-N(1)	2.1586(16)	2.21
Co(1)-N(2)	2.1256(16)	2.19
Co(1)-N(3)	2.1333(16)	2.19
Co(1)-N(4)	2.1383(16)	2.21
Co(1)-O(2)	2.0510(13)	2.08
Co(1)-O(1)	2.0519(14)	2.08
P(1)-O(2)	1.5095(14)	1.54
P(1)-O(1)	1.5089(15)	1.54
P(1)-C(1)	1.807(2)	1.82
O(1)-Co(1)-O(2)	92.31(5)	96
O(1)-P(1)-O(2)	116.16(8)	115
Co(1)-O(2)-P(1)	125.52(7)	131
Co(1)-O(1)-P(1)	135.16(8)	135

Preparation of bis(μ_2-mesitylphosphinato-O,O')tetrakis(2,2'-bipyridine)dicobalt(II) dibromide **1**. 0.11 g (3.0 mmol) of $CoBr_2 \times 6H_2O$, 0.09 g (6.0 mmol) of 2,2'-bipyridine and 0.06 g (3.0 mmol) of mesitylphosphinic acid MesP(O)(OH)H were added to 10 ml of DMF at continuous stirring. The mixture has been stirred for a couple of hours while the clean orange solution was formed. After that resulted mixture has been transferred to a teflon container (volume 20 ml), placed in a closed steel body. Then the container containing reaction mixture was slowly warmed (5 hours) to 120°C and has been kept at this temperature for 25 hours. After cooling the reactor to room temperature (20 h) the teflon container was carefully opened. These

manipulations allow obtaining 0.13 g (yield 68%) of complex **1** as orange crystals suitable for X-ray crystal structure analysis.

Anal. Calcd. $C_{58}H_{56}Br_2Co_2N_8O_4P_2$ (1268.71): C 54.91; H 4.45; Br 12.60; Co 9.29; N 8.83; O 5.04; P 4.88. Found: C 54.93; H 4.46; Br 12.59; Co 9.30; N 8.81; O 5.06; P 4.88.

IR/Raman (cm^{-1}): 3095 w/3075 m, 3052 w/3047 m, 3017/3018 w, 3006 w (ν_{ar}CH); 2922 w/2923 w (ν_{alk}CH); 2396 mw/2396 w (νPH); 1599 s/1598 vs, 1573 w, 1563 w /1565 m, 1490 w/1492 m, 1472 m, 1443 s (bpy); 1422 m, 1378 w (Mes); 1312 m/1316 s (bpy), 1162 vs/1165 vw (ν_{as}OPO), 1102 s/1098 vw (νP-Mes, Mes; 1035 s/1039 vw (ν_{s}OPO); 1018 s/1022 m (bpy); 850 w (Mes), 776 s/766 w (bpy), 738 m (bpy); 626 m/633 vw (bpy).

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