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# First example of neutral dinuclear cobalt complex formed by bridging $[\mu\text{-}O_2P(H)R]^-$ ligands: synthesis, X-ray crystal structure and quantum-chemical study

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All reactions and manipulations were carried out under dry, pure nitrogen using standard Schlenk apparatus. Ethanol was purified by distillation and was stored under an atmosphere of dry nitrogen. 2,2'-Bipyridine (Alfa Aesar), $CoBr_2 \cdot x\ 6H_2O$ (Fluka) are commercially available and were used without additional purification. AntP(O)(OH)H was prepared according to the described procedure.[1]

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 ($\lambda MoK_\alpha$). The structure was solved by direct method using SIR program[2] 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. Hydrogens of P-atoms, located in Fourier maps, were refined isotropically. All calculations were performed using WinGX program.[4] Analysis of intermolecular interactions were performed using PLATON program.[5] All the figures were produced by MERCURY program.[6]

All quantum-chemical computations reported in this study were carried out using the Gaussian 09[7] suite of programs. Calculations were performed with Becke`s exchange functional[8] in combination with Perdew and Wang 1991 gradient-corrected correlation functional[9] (BPW91) as pure GGA; Becke's three parameter hybrid exchange functional[10] and the gradient-corrected nonlocal correlation functional of Lee, Yang and Parr[11] (B3LYP); B3PW91, which uses the PW91 correlation functional[9] instead of LYP, but retains the three parameters derived for B3LYP; and OPBE density functional, which is Handy and Cohen's optimized exchange functional OPTX[12] in combination with Perdew–Burke–Ernzerhof (PBE) functional[13]. The OPBE functional is reported to yield reliable predictions of energy

gaps beyween high and low spin states of different complexes[14]. The ligand atoms H, C, O and P were treated with 6-31G* basis set,[15] while for Co atoms ECP LanL2DZ basis set[16] was used. This level of approximation was shown to produce good results when describing structural and spectroscopic parameters of various organic compounds and their complexes.[17] 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[18] was applied. The selected calculated bond lengths and angles for complex **1** are compared with the corresponding experimental values in Table S1.

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

| | X-ray | B3LYP | |
|---|---|---|---|
| | | HS | LS |
| Co(1)-Br(1) | 2.485(3) | 2.58 | 2.52 |
| Co(1)-N(1) | 2.139(6) | 2.22 | 2.00 |
| Co(1)-N(2) | 2.098(6) | 2.17 | 2.05 |
| Co(1)-O(2) | 1.988(5) | 2.01 | 1.93 |
| Co(1)-O(1) | 1.982(5) | 2.01 | 2.13 |
| P(1)-O(2) | 1.499(5) | 1.54 | 1.55 |
| P(1)-O(1) | 1.490(5) | 1.54 | 1.52 |
| P(1)-C(2) | 1.811(7) | 1.83 | 1.84 |
| O(1)-Co(1)-O(2) | 114.44(19) | 119 | 115 |
| O(1)-P(1)-O(2) | 116.6(3) | 117 | 117 |
| Co(1)-O(2)-P(1) | 139.3(3) | 137 | 140 |
| Co(1)-O(1)-P(1) | 143.1(3) | 134 | 137 |

*Preparation of bis($\mu_2$-anthrylphosphinato-O,O')-bis(2,2'-bipyridine)-dicobalt(II) dibromide (**1**).* 0.65 g (2.0 mmol) of $CoBr_2 \times 6H_2O$, 0.31 g (2.0 mmol) of 2,2'-bipyridine and 0.48 g (2.0 mmol) of 9-anthrylphosphinic acid AntP(O)(OH)H were added to 100 ml of ethanol witht continuous stirring. The mixture has been stirred for a couple of hours to complete dissolving of the added solids, filtered off and the filtrate left for crystallization in inert atmosphere in dark place. These manipulations allow obtaining 0.92 g (yield 43 %) of complex **1** as violet crystals suitable for X-ray crystal structure analysis.

Anal. Calcd. $C_{48}H_{36}Br_2Co_2N_4O_4P_2$ (1072.45) (%): C 53.76; H 3.38; Br 14.90; Co 10.99; N 5.22; P 5.78. Found (%): C 53.78; H 3.41; Br 14.93; Co 11.02; N 5.25; P 5.82.

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