



# First neutral dinuclear cobalt complex formed by bridging $[\mu\text{-O}_2\text{P(H)R}]^-$ ligands: synthesis, X-ray crystal structure and quantum-chemical study

Dmitry G. Yakhvarov,<sup>\*a,b</sup> Ekaterina A. Trofimova,<sup>a</sup> Alexey B. Dobrynin,<sup>a</sup>  
Tatiana P. Gerasimova,<sup>a</sup> Sergey A. Katsyuba<sup>a</sup> and Oleg G. Sinyashin<sup>a</sup>

<sup>a</sup> A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 8432 732253; e-mail: [yakhvar@iopc.ru](mailto:yakhvar@iopc.ru)

<sup>b</sup> A. M. Butlerov Institute of Chemistry, Kazan Federal University, 420008 Kazan, Russian Federation

DOI: 10.1016/j.mencom.2015.01.009

The reaction of cobalt dibromide hexahydrate with 2,2'-bipyridine (bpy) and 9-anthrylphosphinic acid  $\text{AntP(O)(OH)H}$  ( $\text{Ant} = 9\text{-anthryl}$ ) leads to the first example of a neutral dinuclear cobalt(II) complex  $\{\text{Co}_2\text{Br}_2[\mu\text{-O}_2\text{P(H)Ant}]_2(\text{bpy})_2\}$  formed by two bridging  $[\mu\text{-O}_2\text{P(H)Ant}]^-$  ligands. The complex has been characterized by X-ray diffraction analysis and quantum-chemical calculations.

The development of new inorganic and organic materials is the aim of science and technology.<sup>1</sup> After the pioneering works of Tomic<sup>2</sup> and later works of Hoskins and Robson,<sup>3</sup> new types of solid polymeric materials classified as metal-organic frameworks (MOFs) became known.<sup>1</sup> The structure of these polymers includes metal ions linked by organic fragments bonded by  $\sigma$  or  $\pi$  interaction. MOFs are important for gas storage<sup>4</sup> and gas separation<sup>5</sup> devices, nonlinear optics,<sup>6</sup> magnetically active materials,<sup>7</sup> etc.<sup>8</sup> The dinuclear organometallic complexes of  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$  are the important intermediates of biological processes involved in the catalytic hydrolysis of peptides and phosphate esters *via* the formation of  $\{\mu\text{-O-P-O}\}$  bridged organometallic complexes.<sup>9</sup> These species play a central role in oxidative phosphorylation,<sup>10</sup> oxidative decarboxylation<sup>11</sup> and energy transduction.<sup>12</sup> In some cases, they act as catalysts increasing the rate of biological processes by a factor of up to  $10^5$ .<sup>13,14</sup>

However, a very restricted number of dinuclear metal complexes formed by bridging phosphinate  $[\mu\text{-O}_2\text{P(H)R}]^-$  ligands, *i.e.*, bearing the P–H moiety, are currently known.<sup>15</sup> The examples include aluminum,<sup>16</sup> zinc,<sup>17</sup> nickel<sup>18</sup> and cobalt<sup>19</sup> dinuclear complexes. Note that neutral transition metal complexes formed by bridging  $[\mu\text{-O}_2\text{P(H)R}]^-$  ligands were not described, while the P–H bond in a complex molecule can be responsible for catalytic activity in hydrogenation and proton transfer processes.<sup>20</sup>

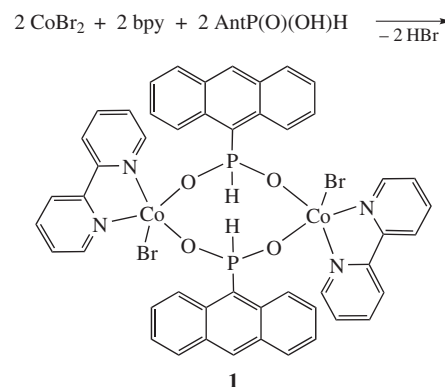
Here, we report the synthesis and crystal structure of neutral dinuclear cobalt complex  $\{\text{Co}_2\text{Br}_2[\mu\text{-O}_2\text{P(H)Ant}]_2(\text{bpy})_2\}$  **1** ( $\text{Ant} = 9\text{-anthryl}$  and  $\text{bpy} = 2,2'\text{-bipyridine}$ ). Complex **1** was prepared in 43% yield at room temperature from 9-anthrylphosphinic acid  $\text{AntP(O)(OH)H}$ ,<sup>18</sup>  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  and 2,2'-bipyridine in ethanol as a solvent (Scheme 1).<sup>†</sup>

According to single-crystal X-ray diffraction data,<sup>‡</sup> complex **1** forms a centrosymmetric dimer in which the two Co atoms are bridged by two  $[\mu\text{-O}_2\text{P(H)Ant}]^-$  ligands (Figure 1). The

<sup>†</sup> For details, see Online Supplementary Materials.

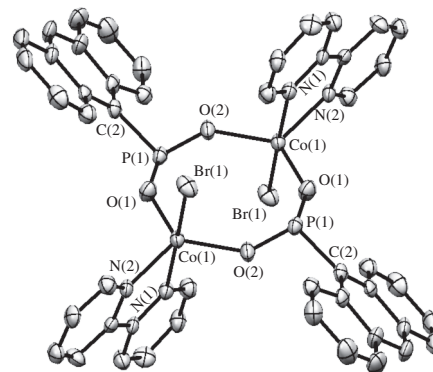
<sup>‡</sup> Crystal data for **1**: purple crystal,  $\text{C}_{48}\text{H}_{36}\text{Br}_2\text{Co}_2\text{N}_4\text{O}_4\text{P}_2$  ( $M = 1072.41$ ), triclinic, space group  $P\bar{1}$ , at 293(2) K:  $a = 10.110(8)$ ,  $b = 10.731(10)$  and  $c = 11.081(10)$  Å,  $\alpha = 89.393(16)^\circ$ ,  $\beta = 86.171(16)^\circ$ ,  $\gamma = 63.180(14)^\circ$ ,  $V = 1070.2(16)$  Å<sup>3</sup>,  $Z = 1$ ,  $d_{\text{calc}} = 1.664$  g cm<sup>-3</sup>,  $\mu = 2.768$  mm<sup>-1</sup>,  $R_{\text{int}} = 0.068$ ,  $\theta_{\text{max}} = 27.0$ . Bruker Smart Apex II CCD diffractometer, 12 103 reflections collected, 3106 observed reflections with  $I > 2\sigma(I)$ , final  $R = 0.0666$ ,  $wR_2 = 0.1876$ , 4633 unique reflections with  $F^2 \geq 2\sigma(I)$ ,  $S = 1.031$ .

CCDC 1023205 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* <http://www.ccdc.cam.ac.uk>.



Scheme 1

P–O–Co-containing eight-membered heterocycles adopt a chair conformation as in cationic cobalt(II) complex  $\{\text{Co}_2[\mu\text{-O}_2\text{P(H)Mes}]_2(\text{bpy})_4\}\text{Br}_2$  **2** ( $\text{Mes} = 2,4,6\text{-trimethylphenyl}$ ) described previously.<sup>19</sup> The cobalt atoms in complex **1** have a slightly distorted trigonal-bipyramidal coordination with a *cis* arrangement of the oxygen atoms, while they display an octahedral coordination in complex **2**. Ant substituents in **1** adopt an almost perpendicular orientation to the P(1)–O(2) bond [torsion angles: O(2)P(1)C(2)C(15),  $-73.0(6)^\circ$  and O(1)P(1)C(2)C(3),  $-27.8(7)^\circ$ ].



**Figure 1** ORTEP view of complex  $\{\text{Co}_2\text{Br}_2[\mu\text{-O}_2\text{P(H)Ant}]_2(\text{bpy})_2\}$  **1** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles ( $^\circ$ ): Co(1)–Br(1) 2.485(3), Co(1)–N(1) 2.139(6), Co(1)–N(2) 2.098(6), Co(1)–O(1) 1.982(5), Co(1)–O(2) 1.988(5), P(1)–O(1) 1.490(5), P(1)–O(2) 1.499(5), P(1)–C(2) 1.811(7); O(1)–Co(1)–O(2) 114.44(19), O(1)–P(1)–O(2) 116.6(3), Co(1)–O(1)–P(1) 143.1(3), Co(1)–O(2)–P(1) 139.3(3).