

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

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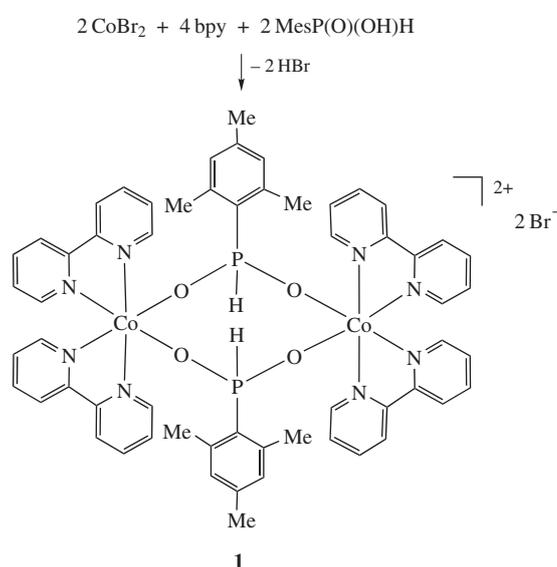
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The reaction of cobalt dibromide hexahydrate with 2,2'-bipyridine (bpy) and mesitylphosphinic acid  $MesP(O)(OH)H$  ( $Mes = 2,4,6$ -trimethylphenyl) under solvothermal synthesis conditions leads to a new dinuclear cobalt(II) complex  $\{Co_2[\mu-O_2P(H)Mes]_2(bpy)_4\}Br_2$  formed by two bridging  $\{\mu-O_2P(H)Mes\}^-$  ligands. X-ray crystal structure analysis of the complex displayed that cobalt ions have distorted octahedral coordination and are doubly bridged by two mesitylphosphinato ligands.

The discovery of new types of materials with practically important properties is one of key strategic trends in the development of chemical science and technology. From this point of view the metal-organic frameworks, or coordination polymers, formed by mono- and polynuclear coordination compounds have become important in various research areas.<sup>1–8</sup> Currently, these compounds are of great interest due to their potential practical applications, mainly as gas-storage<sup>9–12</sup> and magnetically active<sup>13</sup> materials, and frameworks for catalytic reactions.<sup>14–16</sup> Some zinc(II)<sup>17</sup> and magnesium(II)<sup>18</sup> complexes with azo ligands can be regarded as potential building blocks for photogalvanic elements and optical electronic devices.<sup>19–21</sup> Normally, the structural unit is represented as metal centres connected by organic linkers. Dinuclear complexes of nickel(II), zinc(II), cobalt(II) and manganese(II) were found to be important intermediates in biological systems which catalyze hydrolysis of peptide and phosphate ester bonds *via* formation of O–P–O bridged metal intermediates.<sup>22</sup> These species play a central role in biological processes of oxidative phosphorylation,<sup>23,24</sup> oxidative decarboxylation<sup>25</sup> and energy transduction.<sup>26–28</sup> For example, a 60-fold increase in the rate of hydrolysis of adenosine-5'-triphosphate (ATP) is observed in the presence of  $Cu^{II}$  ions, dimeric  $[Cu_2(ATP)_2(OH)_2]^{6-}$  having been found as an intermediate of the overall process.<sup>29</sup> Furthermore, a  $10^5$ -fold acceleration of hydrolysis of pyrophosphates to orthophosphates occurs at pH 7 in the presence of  $[Co(DAP)_2(OH)(H_2O)]^{2+}$  ( $DAP = 1,3$ -diaminopropane) complexes which are converted into dinuclear species.<sup>30</sup>

However, a very restricted number of dinuclear metal complexes formed by bridging phosphinate  $\{\mu-O_2P(H)R\}^-$  ligands bearing P–H moiety are currently known. To the best of our knowledge only aluminum,<sup>31</sup> zinc<sup>32</sup> and nickel<sup>33</sup> dinuclear complexes formed by bridging  $\{\mu-O_2P(H)R\}^-$  ligands have been synthesized and characterized. The presence of P–H bond in the complex molecule can play a central role in its catalytic activity in hydrogenation and proton transfer.<sup>34</sup> Moreover, this creates possibility of direct modification of the obtained polymer at phosphorus centre.

Herein we describe the synthesis and X-ray crystal structure of new dinuclear cobalt complex  $\{Co_2[\mu-O_2P(H)Mes]_2(bpy)_4\}Br_2$  **1** ( $Mes = 2,4,6$ -trimethylphenyl,  $bpy = 2,2'$ -bipyridine), representing the first example of dinuclear cobalt complex formed by bridging mesitylphosphinate ligands. Complex **1** was prepared from 2,4,6-trimethylphenylphosphinic acid,<sup>33,35,36</sup> cobalt dibromide hexahydrate and 2,2'-bipyridine in DMF (Scheme 1).



Scheme 1

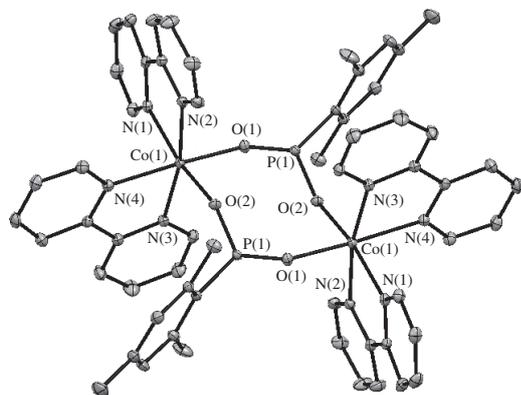
The reactants were dissolved in DMF for 2 h, then the autoclave temperature was raised to 120 °C within 5 h, and the process was run at this temperature for 25 h. After slow (20 h) cooling of the autoclave to room temperature the crystals of **1** suitable for X-ray analysis were obtained in 68% yield.<sup>†</sup> Note that processing at room temperature does not give complex **1** cleanly.

According to single-crystal X-ray diffraction,<sup>‡</sup> cobalt complex **1** forms centrosymmetric dimer in which the two Co atoms are

<sup>†</sup> For detailed procedure and characteristics of complex **1**, see Online Supplementary Materials.

<sup>‡</sup> Crystal data for **1**: brown-yellow crystals,  $C_{58}H_{56}Co_2N_8O_4P_2Br_2$  ( $M = 1268.73$ ), monoclinic, space group  $P2_1/c$ , at 150(2) K:  $a = 11.938(2)$ ,  $b = 15.037(3)$  and  $c = 17.045(3)$  Å,  $\beta = 109.478(2)^\circ$ ,  $V = 2884.9(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{calc} = 1.461$  g cm<sup>-3</sup>,  $\mu = 2.068$  mm<sup>-1</sup>,  $R_{int} = 0.033$ ,  $\theta_{max} = 27.0^\circ$ . Bruker Smart Apex II CCD diffractometer, 24 046 reflections collected, 5382 observed reflections with  $I > 2\sigma(I)$ , final  $R = 0.0271$ ,  $wR_2 = 0.0658$ , 6287 independent reflections with  $F^2 \geq 2\sigma(I)$ ,  $S = 1.03$ .

CCDC 930228 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.



**Figure 1** ORTEP view of the complex dication  $[\text{Co}_2[\mu\text{-O}_2\text{P}(\text{H})\text{Mes}]_2(\text{bpy})_4]^{2+}$  (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles ( $^\circ$ ): Co(1)–N(1) 2.1586(16), Co(1)–N(2) 2.1256(16), Co(1)–N(3) 2.1333(16), Co(1)–N(4) 2.1383(16), Co(1)–O(2) 2.0510(13), Co(1)–O(1) 2.0519(14), P(1)–O(2) 1.5095(14), P(1)–O(1) 1.5089(15), P(1)–C(1) 1.807(2); O(1)–Co(1)–O(2) 92.31(5), O(1)–P(1)–O(2) 116.16(8), Co(1)–O(2)–P(1) 125.52(7), Co(1)–O(1)–P(1) 135.16(8).

bridged by two  $\{\mu\text{-O}_2\text{P}(\text{H})\text{Mes}\}^-$  ligands (Figure 1). The P–O–Co-containing eight-membered heterocycles adopt a chair conformation. The cobalt atoms have slightly distorted octahedral coordination with a *cis*-arrangement of the oxygen atoms. Mesityl substituents are nearly perpendicular in relation to the O–P–O plain.

Analysis of Co–N and Co–O bond lengths allows one to make conclusions about the spin state of Co atoms in **1**. According to B. Cordero *et al.*<sup>37</sup> the estimated covalent radii of Co in low (LS) and high (HS) spin states are 1.26 and 1.50 Å, and covalent radii of O and N are 0.66 and 0.71 Å, respectively. Thus, according to these data  $\text{Co}_{\text{LS}}\text{-N}$  and  $\text{Co}_{\text{LS}}\text{-O}$  bond lengths should be expected to be equal to 1.92 and 1.97 Å, whereas  $\text{Co}_{\text{HS}}\text{-N}$  and  $\text{Co}_{\text{HS}}\text{-O}$  should be expected to be equal to 2.16 and 2.21 Å, respectively. Experimental values 2.13–2.16 Å for Co–N and 2.05 Å for Co–O suggest high spin state for  $\text{Co}^{\text{II}}$  atoms (with  $s = 3/2$ ) in **1**.

IR and Raman spectra of solid samples of the title compound fully correspond to the structure derived from X-ray analysis. The IR bands of bpy vibrations at 1598 and 1443  $\text{cm}^{-1}$  appear to be at least twice more intensive than the band at 1472  $\text{cm}^{-1}$ , which suggests HS state of the metal centre of the complex according to the IR-spectroscopic markers of transition metal spin states published elsewhere.<sup>38</sup> Such interpretation is in agreement with the above discussed Co–N and Co–O bond lengths. To estimate possible interactions between metal centres, quantum-chemical optimizations of HS form of the complex ( $S = 3/2$  for each metal centre,  $M = 7$ ) as well as of ‘broken symmetry’ (BS) state ( $S = 3/2$  for each metal centre,  $M = 1$ ) were carried out. Predicted structural parameters for considered two states are almost identical and agree well with the experimental data (see Online Supplementary Materials). The computations predict almost negligible energy difference of less than 0.01  $\text{kcal mol}^{-1}$  between HS and BS states, which according to Noodleman equation<sup>39</sup> corresponds to extremely weak magnetic coupling between two  $\text{Co}^{\text{II}}$  centres with exchange coupling constant less than 1  $\text{cm}^{-1}$ .

To conclude, the first dinuclear cobalt(II) complex  $\{\text{Co}_2[\mu\text{-O}_2\text{P}(\text{H})\text{Mes}]_2(\text{bpy})_4\}\text{Br}_2$  formed by two  $\{\mu\text{-O}_2\text{P}(\text{H})\text{Mes}\}^-$  bridging ligands is accessed. This type of compounds can be of high interest from the viewpoint of their potential magnetic and catalytic properties.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.05.004.

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