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First neutral dinuclear cobalt complex formed by bridging [μ-$O_2P(H)R]^-$ ligands: synthesis, X-ray crystal structure and quantum-chemical study

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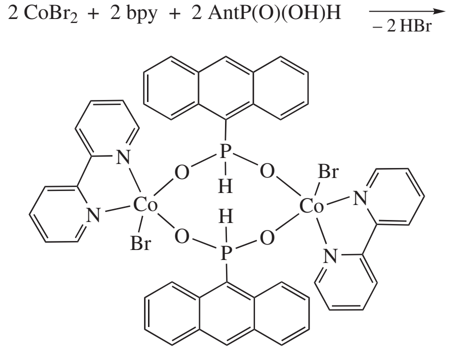
The reaction of cobalt dibromide hexahydrate with 2,2′-bipyridine (bpy) and 9-anthrylphosphinic acid AntP(O)(OH)H (Ant = 9-anthryl) leads to the first example of a neutral dinuclear cobalt(II) complex {Co_2Br_2[μ-$O_2P(H)Ant]_2(bpy)_2$} formed by two bridging [μ-$O_2P(H)Ant]^-$ ligands. The complex has 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.[1] After the pioneering works of Tomic[2] and later works of Hoskins and Robson,[3] new types of solid polymeric materials classified as metal-organic frameworks (MOFs) became known.[1] The structure of these polymers includes metal ions linked by organic fragments bonded by σ or π interaction. MOFs are important for gas storage[4] and gas separation[5] devices, nonlinear optics,[6] magnetically active materials,[7] *etc*.[8] The dinuclear organometallic complexes of Ni^{II}, Zn^{II}, Co^{II} and Mn^{II} are the important intermediates of biological processes involved in the catalytic hydrolysis of peptides and phosphate esters *via* the formation of {μ-O–P–O} bridged organometallic complexes.[9] These species play a central role in oxidative phosphorylation,[10] oxidative decarboxylation[11] and energy transduction.[12] In some cases, they act as catalysts increasing the rate of biological processes by a factor of up to 10^5.[13,14]

However, a very restricted number of dinuclear metal complexes formed by bridging phosphinate [μ-$O_2P(H)R]^-$ ligands, *i.e.*, bearing the P–H moiety, are currently known.[15] The examples include aluminum,[16] zinc,[17] nickel[18] and cobalt[19] dinuclear complexes. Note that neutral transition metal complexes formed by bridging [μ-$O_2P(H)R]^-$ 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.[20]

Here, we report the synthesis and crystal structure of neutral dinuclear cobalt complex {Co_2Br_2[μ-$O_2P(H)Ant]_2(bpy)_2$} **1** (Ant = 9-anthryl and bpy = 2,2′-bipyridine). Complex **1** was prepared in 43% yield at room temperature from 9-anthrylphosphinic acid AntP(O)(OH)H,[18] $CoBr_2 \cdot 6H_2O$ and 2,2′-bipyridine in ethanol as a solvent (Scheme 1).[†]



1

Scheme 1

According to single-crystal X-ray diffraction data,[‡] complex **1** forms a centrosymmetric dimer in which the two Co atoms are bridged by two [μ-$O_2P(H)Ant]^-$ ligands (Figure 1). The P–O–Co-containing eight-membered heterocycles adopt a chair conformation as in cationic cobalt(II) complex {Co_2[μ-$O_2P(H)$-$Mes]_2(bpy)_4\}Br_2$ **2** (Mes = 2,4,6-trimethylphenyl) described previously.[19] 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)° and O(1)P(1)C(2)C(3), –27.8(7)°].

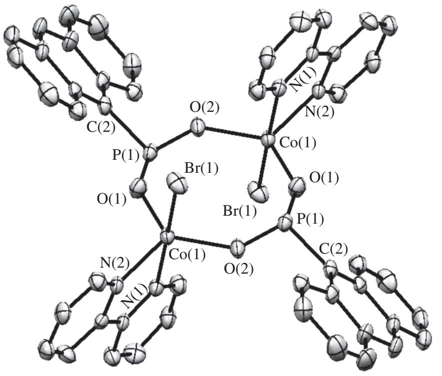


Figure 1 ORTEP view of complex {Co_2Br_2[μ-$O_2P(H)Ant]_2(bpy)_2$} **1** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Co(1)–Br(1) 2.485(3), Co(1)–N(1) 2.139(6), Co(1)–N(2) 2.098(6), Co(1)–O(1) 1.982(5), Co(1)–O(2) 1.988(5), P(1)–O(1) 1.490(5), P(1)–O(2) 1.499(5), 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).

[†] For details, see Online Supplementary Materials.

[‡] *Crystal data for* **1**: purple crystal, $C_{48}H_{36}Br_2Co_2N_4O_4P_2$ (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, α = 89.393(16)°, β = 86.171(16)°, γ = 63.180(14)°, V = 1070.2(16) Å^3, Z = 1, d_{calc} = 1.664 g cm^{-3}, μ = 2.768 mm^{-1}, R_{int} = 0.068, θ_{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 $F^2 \geqslant 2\sigma(I)$, 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.

The analysis of intermolecular interaction showed π–π interactions of bipyridyl fragments. The perpendicular distances from Cg1 to Cg2^{i} [symmetry code: (i) = $1 - x, -y, 1 - z$] and from Cg2 to Cg1^{i} are 3.423 and 3.448 Å, respectively. The centroid-to-centroid distances are 3.610(5) Å (Cg1 to Cg2^{i}) and 3.609(5) Å (Cg2 to Cg1^{i}). Cg1 and Cg2 are the centroids of N(1)–C(16)–C(17)–C(18)–C(19)–C(20) and N(2)–C(21)–C(25)–C(24)–C(23)–C(22) rings, respectively. There are intermolecular π–π [Cg3···Cg3^{ii}] stacking interactions between the centers of anthracene rings with the shortest perpendicular distance of 3.500 Å between the two rings, and the distance between the centroids of the six-membered carbon rings is 3.801(6) Å with the symmetry code ($2 - x, -y, 2 - z$). Cg3 is the centroid of the C(2)–C(3)–C(8)–C(9)–C(10)–C(15) ring.

The binuclear complexes of this type are of interest because of their electronic properties.[7] However, the synthesized complex gave no EPR signal (X-band) at room temperature. This could be a result of the high spin (HS) state of metal atoms in the molecule. To establish the spin state of Co ions in **1**, the Co–O, Co–N and Co–Br bond lengths were analysed. According to Cordero *et al.*[21] the covalent radii of Co in low spin (LS) and HS states are 1.26 and 1.50 Å, respectively. As the covalent radii of O, N and Br are 0.66, 0.71 and 1.20 Å, respectively,[21] the $\mathrm{Co_{LS}}$–O, $\mathrm{Co_{LS}}$–N and $\mathrm{Co_{LS}}$–Br bond lengths are expected to be 1.92, 1.97 and 2.36 Å, respectively, whereas the $\mathrm{Co_{HS}}$–O, $\mathrm{Co_{HS}}$–N and $\mathrm{Co_{HS}}$–Br distances are expected to be 2.16, 2.21 and 2.70 Å, respectively. The actual values of 1.98–1.99 Å for Co–O, 2.10–2.14 Å for Co–N and 2.49 Å for Co–Br bond lengths are intermediate between the above extremes expected for LS and HS states, which suggests that the coexistence of two spin states (with $S = 1/2$ and 3/2) for $\mathrm{Co^{II}}$ ions in a crystal of **1** cannot be excluded.

We considered the LS ($S = 1/2$ for each metal centre, $M = 3$) and HS ($S = 3/2$ for each metal centre, $M = 7$) states of **1** using four different functionals (see Online Supplementary Materials), and all of them yielded qualitatively similar results: the HS state is much more energetically stable (~10–30 kcal mol^{-1} depending on functional) than the LS state. Moreover, the optimization of the starting X-ray geometry results in a distortion of the coordination polyhedron for the LS state, producing a square pyramidal structure with one elongated Co–O bond (Table S1, Online Supplementary Materials), whereas all computations predicted a trigonal bipyramydal environment of the metal centers for the HS state in agreement with the X-ray data. Thus, the quantum-chemical analysis suggests that complex **1** exists in the HS form.

To estimate interactions between the metal centres in **1**, a quantum-chemical optimization of a broken symmetry (BS)[22] state ($S = 3/2$ for each metal centre, $M = 1$) was carried out. Predicted structural parameters for the HS and BS states are almost identical. The computations predicted a negligible energy difference of less than 0.01 kcal mol^{-1} between the HS and BS states, which means very weak magnetic coupling between two $\mathrm{Co^{II}}$ centers.

Thus, the first neutral transition metal complex formed by bridging $[\mu\text{-}\mathrm{O_2P(H)Ant}]^-$ ligands, dinuclear cobalt(II) complex $\{\mathrm{Co_2Br_2}[\mu\text{-}\mathrm{O_2P(H)Ant}]_2(\mathrm{bpy})_2\}$ has been synthesized and characterized by X-ray crystal structure analysis and quantum chemistry.

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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.2015.01.009.

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