A Rare μ_3-η^1,η^2 Peroxo Bridge between Two $Co^{III}Pb^{II}$ Dinuclear Units and Hydrolytic Conversion into a Hydroxo-Bridged $Co^{III}Pb^{II}$ Complex

Hideki Furutachi,* Shuhei Fujinami, Masatatsu Suzuki, and Hisashi Ōkawa*†
Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa 920-1192
†*Department of Chemistry, Graduate School of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581*

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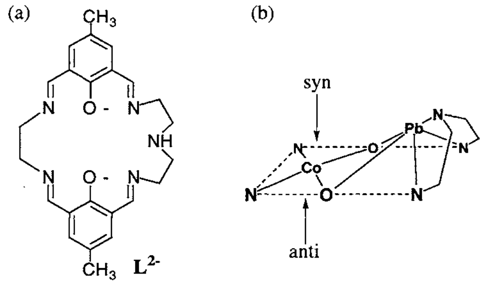
A di(μ-phenoxo)$Co^{II}Pb^{II}$ complex is reversibly oxygenated to form a μ_3–η^1,η^2 peroxo dimer that is hydrolytically converted into a hydroxo–bridged $Co^{III}Pb^{II}$ complex.

The phenol–based compartmental ligand L^{2-} (Scheme 1 (a)), having a "salen"–like N_2O_2 metal–binding site and a "saldien"–like N_3O_2 site sharing the phenolic oxygen, has been developed in our laboratory (Kyushu) for the study of heterodinuclear complexes.[1] Co(salen) is well known for its reactivity toward dioxygen,[2] therefore the dinuclear $Co^{II}M^{II}$ complexes having Co^{II} in the "salen" site of L^{2-} are of great interest in studying the oxygenation at the "Co(salen)" center with respect to a participation of the adjacent M^{II} ion. Here we report oxygenation of a heterodinuclear $Co^{II}Pb^{II}$ complex $[CoPb(L)(CH_3OH)](ClO_4)_2$ (**1**) derived from the macrocycle L^{2-} to form a rare μ_3–η^1,η^2 peroxo complex. The synthesis and structure of **1** were reported previously.[3] It has a non–planar core structure providing non–equivalent *anti* and *syn* sites for oxygenation at the Co center (Scheme 1(b)).



Scheme 1. Chemical structure of L^{2-} (a) and two possible oxygenation site of **1** (b).

Complex **1** in dry acetonitrile reacted with dioxygen at 0 °C with an instantaneous colour change from red to dark red. The resulting dark red solution was EPR–silent, suggesting the formation of a peroxo complex in the solution. Upon warming the oxygenated solution up to 25 °C, deoxygenation occurred to give the original red colour.[4] Thus, **1** acts as a reversible dioxygen carrier by the control of temperature.

The dioxygen adduct $[\{CoPb(L)(CH_3CN)\}_2(O_2)](BPh_4)_2(ClO_4)_2 \cdot 4CH_3CN \cdot 5.5H_2O$ (**2**) was isolated as single crystals when an acetonitrile solution of **1** was oxygenated at –30 °C in the presence of excess $NaBPh_4$ and diffused with diethyl ether.[5] Since the precision of X-ray analysis for **2** is not satisfied owing to the limited number of reflections, detailed discussion of the bond distances and angles may not be made, but the present result is useful for discussing the structural feature. The structure of the cationic part of **2** is given in Figure 1. The Co ion resides in the "salen" site and the Pb ion in the "saldien" site. The peroxide ion makes bonds through O(1) to Co(1) and Pb(1) of one dinuclear unit and through O(2) to Co(2) of another dinuclear unit, providing a μ_3–η^1,η^2 peroxo complex. The O(1)–O(2) bond distance is 1.35(2) Å, which is reasonable value compared with that of the μ–η^1,η^1 peroxo complexes of Co(salen) (1.383(7) – 1.339(6) Å).[2,6] Two CoPb(L) units are stacked by one of the phenolate entities with the average separation of 3.6 Å (see Figure 1).

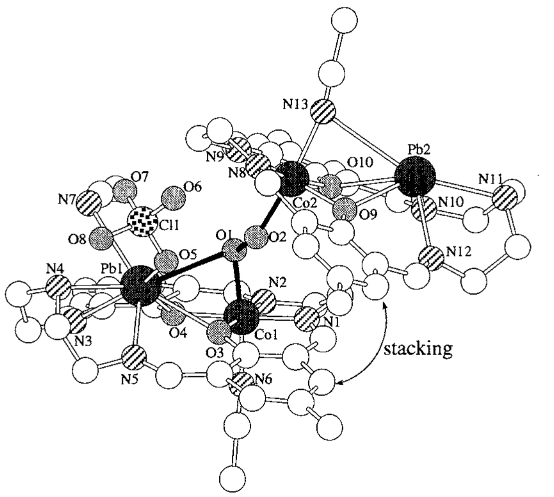


Figure 1. Perspective view of **2**. Selected bond distances (Å) and angles (°): O(1)–O(2) 1.35(2), Co(1)···Pb(1) 3.460(4), Co(2)···Pb(2) 3.452(4), Co(1)···Co(2) 4.368(6), Co(1)–O(1) 1.92(2), Co(1)–N(6) 1.93(2), Co(1)–L 1.86(3)–1.94(2), Co(2)–O(2) 1.88(2), Co(2)–N(13) 2.08(3), Co(2)–L 1.84(3)–1.92(2), Pb(1)–O(1) 3.12(2), Pb(1)–O(5) 3.09(3), Pb(1)–N(7) 3.06(4), Pb(1)–L 2.51(2)-2.62(3), Pb(2)–N(13) 3.20(2), Pb(2)–L 2.49(2)–2.62(2); Co(1)–O(1)–O(2) 114(1), Co(2)–O(2)–O(1) 117(1), Co(1)–O(1)–O(2)–Co(2) 137(1).

Because of the unsymmetric bridge of the peroxide ion, the two macrocyclic CoPb units of **2** are not equivalent. In one unit, the Co(1) and Pb(2) ions are bridged by the peroxo oxygen O(1), along with the two phenolic oxygens of L^{2-}. The geometry about Co(1) is pseudo octahedral with the N_2O_2 donor atoms of the "salen" site on the base and the peroxo oxygen O(1) and the acetonitrile nitrogen N(6) at the axial positions. The geometry about Pb(1) is of an eight–coordination with the N_3O_2 donor atoms of the "saldien" site, the bridging peroxo oxygen O(1), the acetonitrile nitrogen N(7), and the perchlorate oxygen O(5). In another unit, the Co(2) and Pb(2) ions are bridged by the acetonitrile nitrogen N(13), along with the two phenolic oxygens of L^{2-}.

In the CoPb complex of L^{2-}, the axial coordination of an oxygenic donor to the Co in the "salen" site preferentially occurs at the *syn* site so as to interact with the adjacent Pb ion.[3,7]

Thus, the *syn–syn* $(\mu_4\text{–}\eta^2,\eta^2)$ peroxo bridge was thought to be preferred to the *anti–syn* $(\mu_3\text{–}\eta^1,\eta^2)$ and *anti–anti* $(\mu\text{–}\eta^1,\eta^1)$ bridge. X-ray crystallography indicates that the oxygenation occurs at the *syn* site of the Co in the Co(1)Pb(1) unit whereas at the *anti* site in the Co(2)Pb(2) unit to give the *anti–syn* bridge. The *anti–syn* peroxo bridge is inevitably formed in this case because the *syn–syn* peroxo bridge gives rise to a spatial contact between the two CoPb entities within a molecule.

The ^{1}H NMR spectrum of oxygenated complex of **1** in d_3–acetonitrile shows a total of eight resonances which are classified into four singlet pairs (in the range of 6.5–9.5 ppm) based on ^{13}C–^{1}H COSY and DEPT studies ((i) 8.87 and 8.48, (ii) 7.68 and 7.15, (iii) 7.52 and 7.04, (iv) 7.27 and 6.81 ppm). The signals (i) and (ii) are attributed to the non–equivalent azomethine protons and the signals (iii) and (iv) to the non–equivalent ring protons. Some resonances (8.48, 7.68, 7.15, 7.27, 7.04 and 6.81 ppm) exhibit a significant upfield shift relative to that of a corresponding monomeric Co$^{\mathrm{III}}$Pb$^{\mathrm{II}}$ complex.[7] Evidently, the two CoPb units are held in a stacked form and the free rotation of the units with respect to the peroxo bridge is inhibited within NMR time scale owing to the $\mu_3\text{–}\eta^1,\eta^2$ peroxo bridge.

It must be noted that there is a remarkable difference in oxygenation between Co(salen) and **1**; Co(salen) forms a peroxo complex in coordinative solvents such as dmf or pyridine at high concentration,[8] whereas the formation of **2** occurs even in weak coordinative solvents such as acetonitrile or acetone at low concentration. Thus, the formation of **2** is ascribed to a neighbouring effect of the Pb as seen in the $\mu_3\text{–}\eta^1,\eta^2$ peroxo bridge and the stacking interaction between the phenolate entities as confirmed by X-ray and NMR analyses.

The peroxo complex **2** is stable in dry acetonitrile, however, we have found that **2** is converted into a Co$^{\mathrm{III}}$(OH)Pb$^{\mathrm{II}}$ species in a hydrous solution. The ^{1}H NMR spectrum of the Co$^{\mathrm{III}}$(OH)Pb$^{\mathrm{II}}$ species shows four singlets due to the two azomethine (8.62 and 8.11 ppm) and two aromatic ring protons (7.61 and 7.53 ppm) of L^{2-} when a small amount of D_2O was added to a d_3–acetonitrile solution of **2** at −20 °C. When a hydrous acetonitrile solution of **2** was diffused with diethyl ether in the presence of excess $NaBPh_4$ at −30 °C, single crystals of $[CoPb(L)(OH)(CH_3CN)_2](BPh_4)_2\cdot 2.5H_2O$ (**3**) were obtained.[9]

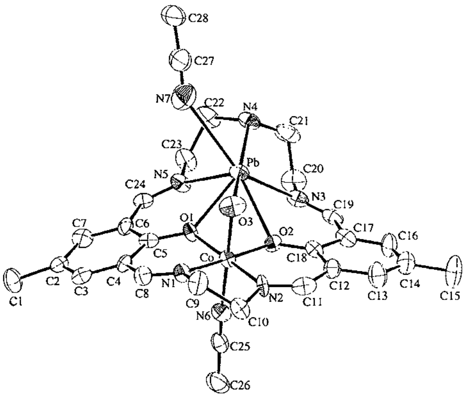


Figure 2. Perspective view of **3**. Selected bond distances (Å) and Angles(°): Co···Pb 3.423(2), Co–O(1) 1.90(1), Co–O(2) 1.88(1), Co–O(3) 1.87(1), Co–N(1) 1.87(1), Co–N(2) 1.87(1), Co–N(6) 1.95(2), Pb–O(1) 2.540(10), Pb–O(2) 2.624(10), Pb–O(3) 2.98(1), Pb–N(3) 2.53(1), Pb–N(4) 2.61(1), Pb–N(5) 2.53(1), Pb–N(7) 3.04(2); O(3)–Co–N(6) 175.3(6), Co–O(1)–Pb 99.9(4), Co–O(2)–Pb 97.5(4), Co–O(3)–Pb 86.7(5).

The structure of the cationic part of **3** is given in Figure 2. It has a discrete CoPb core bridged by a hydroxo oxygen O(3), along with the phenolic oxygens O(1) and O(2) of L^{2-}, in the Co--Pb intermetallic separation of 3.423(2) Å. The hydroxo group is bound to the *syn* site of the Co and makes a bridge to the adjacent Pb. The Co–O(3) and O(3)–Pb bond distances are 1.87(1) and 2.98(1) Å, respectively. We have confirmed that hydrogen peroxide is produced in the hydrolytic conversion by iodometric method.[10] Thus, the conversion of **2** into **3** is represented as $[\{CoPb(L)\}_2(O_2)]^{4+} + 2H_2O \rightarrow 2[CoPb(L)(OH)]^{2+} + H_2O_2$. One of possible origin for this reaction is attributable to the role of Pb as Lewis acid to provide OH$^-$, leading to the hydrolytic conversion of peroxo complex **2** into hydroxo complex **3**.

In conclusion, the Pb ion in complex **1** exerts a neighbouring effect upon the oxygenation at the Co center to provide the $\mu_3\text{–}\eta^1,\eta^2$ peroxo dimer **2**, that is irreversible converted in hydrous solution into the hydroxo–bridged Co$^{\mathrm{III}}$Pb$^{\mathrm{II}}$ complex **3**.

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References and Notes

1 H. Ōkawa, H. Furutachi, and D. E. Fenton, *Coord. Chem. Rev.*, **174**, 51 (1998) and references therein. Abbreviations used: H_2salen = bis(salicylidene)ethylenediamine; H_2saldien = bis(salicylidene)–diethylenetriamine.
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4 UV–vis data [conc. 1 × 10^{-3} M; λ / nm (ε / M^{-1} cm^{-1})] for **1** in acetonitrile at 25 °C, 370 (9500), 420 (sh), 540 (1200); for the oxygenated solution, 392 (11200), 560 (1500) at 0 °C.
5 Crystal data for **2** at −120 °C; $C_{108}H_{105}B_2Co_2Cl_2N_{16}O_{19.5}Pb_2$, orthorhombic, space group *P*bca with $Z = 8$, $a = 44.812(7)$, $b = 27.865(7)$, $c = 18.344(3)$ Å, $V = 22906(8)$ Å^3, $D_c = 1.487$ g cm^{-3}, $R = 0.065$, $R_w = 0.071$ for 4731 data with $I > 3\sigma(I)$.
6 In spite of many efforts no convincing assignment of ν(O–O) and ν(M–O) modes for **2** could be made by resonance Raman spectroscopy.
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9 Crystal data for **3** at −120 °C; $C_{76}H_{79}B_2CoN_7O_{5.5}Pb$, monoclinic, space group $P2_1/n$ with $Z = 4$, $a = 13.390(3)$, $b = 28.422(7)$, $c = 23.024(9)$ Å, $\beta = 101.193(2)°$, $V = 8595(3)$ Å^3, $D_c = 1.140$ g cm^{-3}, $R = 0.086$, $R_w = 0.147$ for 8842 data with $I > 3\sigma(I)$.
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