A Macrocyclic Co(II)Pb(II) Complex: Neighboring Pb(II) Effect upon Reversible Superoxo-cobalt Complex Formation in Solid State

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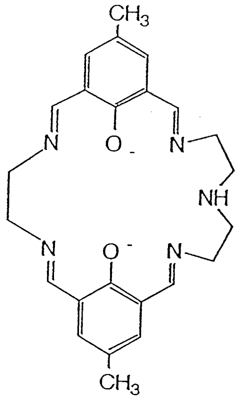
(Received August 9, 1996)

A diphenoxo-bridged Co(II)Pb(II) complex of a dinucleating macrocycle, derived from the [2:1:1] condensation of 2,6-diformyl-4-methylphenol, ethylenediamine and diethylenetriamine, forms a reversible dioxygen-adduct in solid state.

The phenol-based dinucleating macrocycle $(L)^{2-}$, having two dissimilar coordination sites of N_2O_2 and N_3O_2 donor sets sharing the phenolic oxygens (Scheme 1), has been developed in our laboratory.[1,2] It forms a series of discrete heterodinuclear complexes with Cu(II) or Ni(II) ion at the N_2O_2 site and Pb(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II) ion at the N_3O_2 site. One of our objects using $(L)^{2-}$ and related macrocycles[3] is to provide heterodinuclear core complexes of functional significance. In this context the dinuclear complexes with Mn(II), Fe(II) or Co(II) ion at the N_2O_2 site are of particular interest because the salen (N,N'-disalicylidene-ethylenediaminate) complexes of these ions are highly reactive toward molecular dioxygen.[4-6] Here we report a Co(II)Pb(II) complex of the macrocycle $[CoPb(L)CH_3OH](ClO_4)_2$ in which the Pb(II) shows a unique neighboring effect upon a reversible superoxo-cobalt complex formation in solid state.



Scheme 1. Chemical structure of the macrocycle $(L)^{2-}$.

Air-sensitive N,N'-ethylenedi(3-formyl-5-methylsalicylidene)aminatocobalt(II) was prepared according to the literature method.[1] This complex was reacted with diethylenetriamine in the presence of lead(II) perchlorate trihydrate in an atmosphere of nitrogen to give $[CoPb(L)CH_3OH](ClO_4)_2$ (mono-methanol adduct) as orange microprisms.[7] Slow diffusion of 2-propanol into a methanolic solution of the mono-methanol adduct formed large crystals of the di-methanol adduct $[CoPb(L)CH_3OH](ClO_4)_2 \cdot CH_3OH$ suitable for X-ray crystallography.[8] An ORTEP view of the complex is shown in Figure 1.

The complex consists of the macrocycle $(L)^{2-}$, a Co(II) ion, a Pb(II) ion, a methanol molecule and two perchlorate ions. One of the methanol molecules is free from coordination and captured in the lattice. The Co and Pb ions are bridged by the phenolic oxygens, O1 and O2, with the intermetallic separation of 3.468(1) Å. The Co(II) ion resides at the N_2O_2 site of the macrocycle and assumes a square-pyramidal geometry together with the methanol oxygen O3 at the axial site. The basal Co-N and Co-O bond distances fall in the range of 1.871(6)-1.901(4) Å which are short relative to the Cu-N and Cu-O bond distances of the Cu(II)Pb(II) and Cu(II)Mn(II) complexes of $(L)^{2-}$.[1] Such short Co-N and Co-O bond distances are in accord with the low-spin electronic configuration of the Co(II) ion (μ_{eff} for the mono-methanol adduct: 2.32 μ_B at 290 K). The axial Co-O3 bond is significantly elongated (2.261(5) Å).

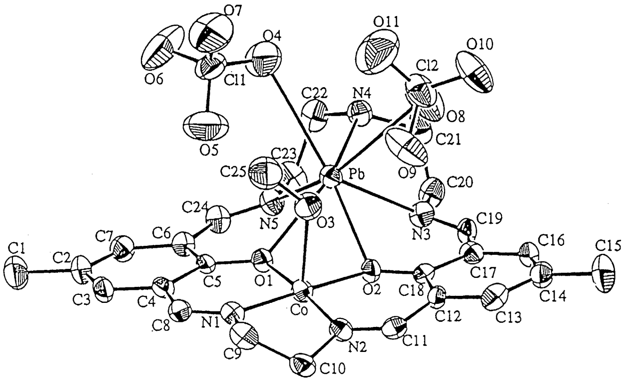


Figure 1. ORTEP drawing of $[CoPb(L)(CH_3OH)](ClO_4)_2 \cdot CH_3OH$. Selected bond distances (Å): Co-O1 1.895(4), Co-O2 1.901(4), Co-O3 2.261(5), Co-N1 1.882(5), Co-N2 1.871(6), Pb-O1 2.589(4), Pb-O2 2.660(4), Pb-O4 3.088(6), Pb-O8 2.944(6), Pb-N3 2.528(5), Pb-N4 2.575(5), Pb-N5 2.472(5).

The Pb(II) ion at the N_3O_2 site has a seven-coordinate geometry together with two perchlorate oxygens. The Pb is 1.38 Å deviated from the least-squares plane defined by O1, O2, N3 and N5 because of its large ionic radius. The deviation of the Pb from the basal N_2O_2 plane and the coordination of two perchlorate groups to the Pb ion provide a large cavity above the Co(II) ion, allowing the coordinative incorporation of one methanol molecule in the cavity.

In the bulk two CoPb complexes stack at the "Co(salen)" entity with the average interatomic separation of 3.5 Å. The Co--Co' separation is 3.506(2) Å and there is the inversion center at the midpoint of Co--Co'.

The ESR spectrum of the mono-methanol adduct (on powdered sample at liquid nitrogen temperature) shows a rhombic pattern with $g_x = 2.98$, $g_y = 2.20$, $g_z = 2.04$, $A_x = 113$ G (gauss = 10^{-4} T), $A_y = 118$ G and $A_z = 156$ G (see Figure 2 (a)). The spectral feature is typical of the low-spin d^7 configuration of the $(d_{z^2})^1$ ground-state largely separated from other excited states.[9,10] This fact means a weak antibonding nature of the bridging phenolic oxygen in the CoPb complex relative

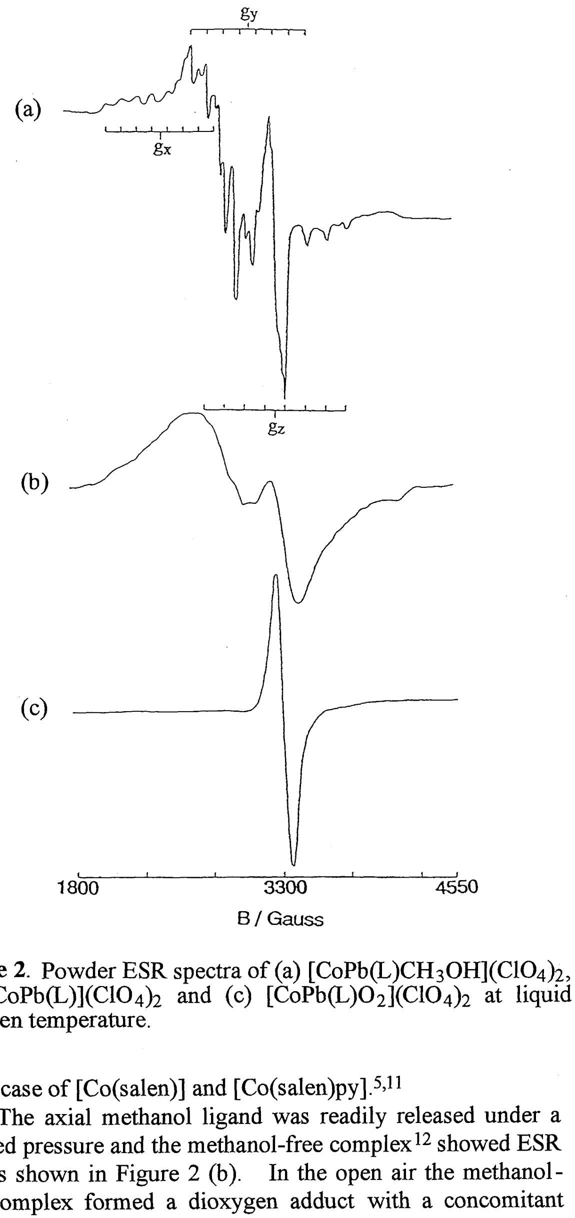


Figure 2. Powder ESR spectra of (a) $[CoPb(L)CH_3OH](ClO_4)_2$, (b) $[CoPb(L)](ClO_4)_2$ and (c) $[CoPb(L)O_2](ClO_4)_2$ at liquid nitrogen temperature.

to the case of [Co(salen)] and [Co(salen)py].[5,11]

The axial methanol ligand was readily released under a reduced pressure and the methanol-free complex[12] showed ESR signals shown in Figure 2 (b). In the open air the methanol-free complex formed a dioxygen adduct with a concomitant color change from orange to dark brown. Analytical results suggest the formation of $[CoPb(L)O_2](ClO_4)_2$.[13] The same dioxygen adduct was obtained when the mono-methanol adduct was allowed to stand in open air. The dioxygen adduct shows an isotropic ESR signal of a narrow band width at g~2.01 (Figure 2 (c)), typical of a superoxocobalt(III) complex[5,11] though Co hyperfine structures are not resolved. The room-temperature magnetic moment of the dioxygen adduct is 1.89 μ_B that is also consistent with the Co(III)-O_2^- formalism. Its ν(O-O) mode, expected to appear in the region of 1150-1090 cm^{-1},[14] is concealed by the intense ν_3 mode of perchlorate ion. When heated at 80 °C *in vacuo*, the dioxygen-adduct was converted into $[CoPb(L)](ClO_4)_2$ showing the ESR spectrum of Figure 2 (b). Thus, the CoPb complex acts as a reversible O_2-carrier in solid state.

It must be emphasized that the CoPb complex does not show such oxygenation in solution at room temperature. In fact the dioxygen adduct was deoxygenated in acetonitrile or DMF. All these facts indicate that the cavity constructed over the Co(II) plays an essential role in incorporating dioxygen at ambient temperature. Thus, the present study illustrates a neighboring effect of the adjacent ion upon functions of hetero-dinuclear system.

We thank Associate Professor H. Sakiyama of Yamagata University for helpful discussion. This work was supported by a Grant-in-Aid for Scientific Research (No. 07454178) from the Ministry of Education, Science and Culture, Japan.

References and Notes

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7 Found for $[CoPb(L)CH_3OH](ClO_4)_2$: C, 32.99; H, 3.25; N, 7.82; Co, 7.10%. Calcd for $C_{25}H_{31}Cl_2CoN_5O_{11}Pb$: C, 32.83; H, 3.42; N, 7.66; Co, 6.40%.

8 Crystal data for $[CoPb(L)CH_3OH](ClO_4)_2 \cdot CH_3OH$ at 273 K. Orange prisms, orthorhombic, space group Pbca (No.61) with Z = 8, a = 19.985(5), b = 19.711(2), c = 16.547(3) Å, V = 6518(1) Å^3, Z =8, D_c = 1.93 g cm^{-3}, *F(000)* = 3720.0, μ(MoKα)=59.09 cm^{-1}. Cell parameters were defined by 25 reflections with 28.0 < 2θ < 29.9°. 6351 unique reflections were measured with $2\theta_{max} = 50°$. All the measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71069) and a 12 kW rotation anode generator. The structure was solved, expanded and refined using the teXsan crystal-lographic software package from Molecular Structure Corporation. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement based on 3737 observed reflections (I≥3σ(I)) converged with R =0.032 and R_w =0.023. Atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen coordinates of $[CoPb(L)CH_3OH](ClO_4)_2$ - H_3OH are deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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12 Found for $[CoPb(L)](ClO_4)_2$: C, 32.43; H, 3.20; N, 7.86; Co, 6.41%. Calcd for $C_{24}H_{27}Cl_2CoN_5O_{10}Pb$: C, 32..66 H, 3.08; N, 7.94; Co, 6.68%.

13 Found for $[CoPb(L)(O_2)](ClO_4)_2$: C, 31.40; H, 3.35; N, 7.47; Co, 6.21%. Calcd for $C_{24}H_{27}Cl_2CoN_5O_{12}Pb$: C, 31.52 H, 2.98; N, 7.66; Co, 6.44%.

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