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Dioxygen Oxidation of Coordinated Nitrosyl to Nitro on Dmf-Bridged Dinuclear CoPb Complex

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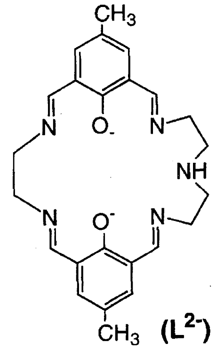
The $Co^{II}Pb^{II}$ complex $[CoPb(L)(CH_3OH)(ClO_4)_2]$ reacts with nitrogen monoxide to give the nitrosyl complex $[CoPb(L)(NO)(dmf)_2(ClO_4)]ClO_4$ (**1**), where H_2L is a dinucleating macrocycle derived from the [2 : 1 : 1] condensation of 2,6-diformyl-4-methylphenol, ethylenediamine, and diethylenetriamine and has a "salen"- and a "saldien"-like metal-binding site sharing the phenolic entities. **1** crystallizes in the triclinic space group $P\bar{1}$, $a = 12.729(4)$, $b = 17.103(6)$, $c = 10.548(4)$ Å, $\alpha = 107.42(4)^\circ$, $\beta = 106.18(2)^\circ$, $\gamma = 101.33(3)^\circ$, $V = 2003(1)$ Å^3, and $Z = 2$. The refinement converges with $R = 0.045$ and $R_w = 0.049$ for 3768 reflections with $I > 3.00\sigma(I)$. The Co resides in the "salen" site and the Pb in the "saldien" site. The metal ions are bridged by the two phenolic oxygens of L^{2-} and a dmf oxygen, in the Co–Pb intermetallic separation of 3.511(2) Å. The Co–O(dmf) and O(dmf)–Pb bond distances are 2.14(1) and 3.072(8) Å, respectively. The NO coordinates to the Co at the axial site *trans* to the bridging dmf oxygen, providing a six-coordinate geometry about the metal; the Co–N(nitrosyl) distance is 1.92(1) Å and the Co–N–O angle is 117(1)°. The Pb has an eight-coordinate geometry together with the bridging dmf oxygen, a terminal dmf oxygen and a perchlorate oxygen. The nitrosyl complex **1** is oxidized with molecular oxygen to the nitro complex $[CoPb(L)(NO_2)(dmf)_2(ClO_4)]ClO_4$ (**2**). **2** crystallizes in the triclinic space group $P\bar{1}$, $a = 12.748(4)$, $b = 17.139(5)$, $c = 10.359(3)$ Å, $\alpha = 106.34(3)^\circ$, $\beta = 106.44(3)^\circ$, $\gamma = 101.42(3)^\circ$, $V = 1986(1)$ Å^3, and $Z = 2$. The refinement converges with $R = 0.039$ and $R_w = 0.042$ based on 6202 reflections with $I > 3.00\sigma(I)$. **2** has a dinuclear core very similar to that of **1**, bearing an NO_2 group instead of an NO group. The Co–N(nitro) bond distance is 1.889(6) Å. ^1H NMR, ^{13}C NMR, and ^{13}C–^1H COSY spectroscopies indicate that the dmf-bridged dinuclear cores of **1** and **2** are retained in solution.

Nitrosyl metal complexes have been extensively studied from the viewpoint of basic coordination chemistry,[1)] interaction of nitrogen monoxide (NO) with biomolecules such as hemoglobin and myoglobin,[2)] and relevance to metallobiosites such as nitrite reductase and bacterial or fungal nitrogen monoxide reductase.[3)] It is known that planar cobalt(II) complexes of quadridentate Schiff bases react with nitrogen monoxide to form nitrosyl cobalt complexes,[4)] and the oxidative conversions of the NO cobalt complexes to nitro or nitrato complexes are reported.[5)] X-Ray crystallographic studies have been made for [Co(salen)NO][6)] (H_2salen; *N*,*N*′-ethylenedisalicylidenediamine) and [Co(acacen)NO][7)] (H_2acacen;bis(acetylacetone)ethylenediimine), but the corresponding nitro and nitrato cobalt complexes were not determined in the crystal structure.

The dinucleating macrocycle derived from the [2 : 1 : 1] condensation of 2,6-diformyl-4-methylphenol, ethylenediamine, and diethylenetriamine (see Scheme 1, abbreviated as L^{2-}) has a "salen"-like metal-binding site and a "saldien"-like site sharing the phenolic entities and can provide discrete heterodinuclear core complexes.[8)] Heterodinuclear complexes having Co^{II}, Fe^{II} or Mn^{II} ion in the "salen" site are of particular interest because salen complexes of these metal ions are sensitive towards small molecules such as O_2 and NO.[4,9)] In our previous studies on a $Co^{II}Pb^{II}$ complex, we showed that the oxygenation on the Co ion in the "salen" site is affected by the neighbouring Pb ion in the "saldien" site.[8c)]


Scheme 1.

In this study, a nitrosyl complex $[CoPb(L)(NO)(dmf)_2(ClO_4)]ClO_4$ (**1**) has been obtained by the reaction of $[CoPb(L)(CH_3OH)(ClO_4)_2]$[8c)] with nitrogen monoxide (NO). The nitrosyl complex is oxidized with dioxygen into a nitro complex $[CoPb(L)(NO_2)(dmf)_2(ClO_4)]ClO_4$ (**2**). X-Ray crystallography and NMR spectroscopies for **1** and **2** demonstrate a dmf-bridge between the Co and Pb ions through its oxygen and the dmf-bridging effect upon the oxidative conversion of **1** to **2** is discussed.

Experimental

Measurements. Elemental analyses of C, H, and N were obtained from the Service Centre of Elemental Analysis at Kyushu University. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer using KBr disks. Electronic spectra were measured in dmf on a Shimadzu UV-210 spectrophotometer at room temperature. Molar conductances were measured in dmf on a DKK AOL-10 conductivity meter at ambient temperature. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-SX102A/102A BE/BE four-sector type tandem mass spectrometer using nitrobenzylalcohol as the matrix. ^{1}H NMR, ^{13}C NMR, and ^{13}C–^{1}H COSY spectra were recorded on a JEOL JNM-GX 400 spectrometer using tetramethylsilane (TMS) as the internal standard.

Materials. Unless otherwise stated, all chemicals were purchased from commercial sources and used without further purification. Solvents were purified and dried by standard methods. Deuteriated solvents d_7-dmf (99.5%, Aldrich) and D_2O (99.8%, Merk) were commercially obtained. Nitrogen monoxide and oxygen were purchased from Nippon Sanso Co.

Preparations. 2,6-Diformyl-4-methylphenol was prepared by the literature method.[10] The synthesis of $[CoPb(L)(CH_3OH)(ClO_4)_2]$ was described in our previous paper.[8c] All the operations for syntheses were carried out in a nitrogen atmosphere using a glove box from Vacuum Atmospheres Company Model MO-40-IV or in an argon atmosphere using a standard Schlenk apparatus.

[CoPb(L)(NO)(dmf)₂(ClO₄)]ClO₄ (1). $[CoPb(L)(CH_3OH)(ClO_4)_2]$ (0.365 g, 0.4 mmol) was dissolved in acetonitrile (50 cm^3) and nitrogen monoxide (NO) gas was bubbled into the solution for 10 min at room temperature. The colour of the solution immediately changed from red to dark green. The reaction mixture was evaporated to dryness, the resulting crude product was taken up with dmf, and the solution was layered with 2-propanol to form dark brown prisms. The yield was 0.36 g (85%). Anal. Calcd for $C_{30}H_{41}Cl_2CoN_8O_{13}Pb$: C, 34.03; H, 3.90; N, 10.58%. Found: C, 33.84; H, 3.87; N, 10.42%. FAB mass: *m/z* 813 for $\{CoPb(L)(NO)(ClO_4)\}^+$. Selected IR data [ν/cm^{-1}] using KBr disks: 3320, 2930, 2850, 1680, 1640, 1140, 1100. Molar conductance [Λ_M/Scm^{2}mol^{-1}] in dmf: 148. UV-vis data [λ/nm (ε/M^{-1} cm^{-1})] in dmf: 390 (11200), 580 (290).

[CoPb(L)(NO₂)(dmf)₂(ClO₄)]ClO₄ (2). The nitrosyl complex **1** (0.423 g, 0.4 mmol) was dissolved in dmf (10 cm^3) and molecular dioxygen was bubbled into the solution for 10 minutes at room temperature. The mixture was allowed to stand for 1 d and layered with 2-propanol to form dark brown prisms. The yield was 0.24 g (56%). Anal. Calcd for $C_{30}H_{41}Cl_2CoN_8O_{14}Pb$: C, 33.53; H, 3.85; N, 10.43%. Found: C, 33.96; H, 3.94; N, 10.83%. FAB mass: *m/z* 829 for $\{CoPb(L)(NO_2)(ClO_4)\}^+$. Selected IR data [$\nu$/cm^{-1}] using KBr disks: 3310, 2930, 2850, 1640, 1438, 1310, 1140, 1100, 810. Molar conductance [Λ_M/S cm^2 mol^{-1}] in dmf: 134. UV-vis data [λ/nm (ε/M^{-1} cm^{-1})] in dmf: 390 (13500), 580 (330).

X-Ray Crystallography. Each single crystal of **1** and **2** was mounted on a glass fiber and coated with epoxy resin. Measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo *Kα* radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. The data were collected at 20±1°C using an ω–2θ scan technique to a maximum 2θ value of 45.0° for **1** and 55.0° for **2** at a scan speed of 16.0° min^{-1} (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 4 scans for **1** and 5 scans for **2**) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 235 mm, and the computer-controlled detector aperture was set to 9.0×13.0 mm (horizontal×vertical). The intensities of three representative reflections were measured after every 150 reflections. Over the course of the data collection, the standard reflections were monitored and the decay corrections were applied by a polynomial correction. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by a direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but not refined. Full-matrix least-squares refinements were based on observed reflections with $I > 3.00\sigma(I)$. The unweighted and weighted agreement factors were defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Plots of $\Sigma w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. For **1**, the nitrosyl oxygen is disordered in two equivalent sites and the two oxygens were assigned 0.5 occupancy. These atoms were refined with anisotropic thermal parameters. Crystal data and details of the structure determinations are summarized in Table 1.

Neutral atom scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_{calcd};[12] the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[13] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[14] All the calculations were performed on an IRIS Indigo computer using the teXsan crystallographic software package of Molecular Structure Corporation.[15] The final atomic coordinates, thermal parameters, full bond distances and angles and tables were deposited as Docment No. 71015 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystallographic Data for $[CoPb(L)(X)(dmf)_2(ClO_4)]ClO_4$ (X = NO (**1**), NO_2 (**2**))

	1 (NO)	**2** (NO₂)
Formula	$C_{30}H_{41}Cl_2CoN_8O_{13}Pb$	$C_{30}H_{41}Cl_2CoN_8O_{14}Pb$
FW	1058.74	1074.74
Crystal color	Brown	Brown
Crystal size/mm	0.2 × 0.2 × 0.25	0.2 × 0.2 × 0.2
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.729(4)	12.748(4)
b/Å	17.103(6)	17.139(5)
c/Å	10.548(4)	10.359(3)
α/deg	107.42(4)	106.34(3)
β/deg	106.18(2)	106.44(3)
γ/deg	101.33(3)	101.42(3)
V/Å^3	2003(1)	1986(1)
Z	2	2
D_{calcd}/g cm^{-3}	1.755	1.797
λ (Mo *Kα*)/Å	0.71069	0.71069
No. of reflections	5745	9548
R[a]	0.045	0.039
R_w[b,c]	0.049	0.042

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R_w = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma[w|F_o|^2]\}^{1/2}$. c) $w = 1/\sigma^2(F_o)$.

Results and Discussion

Preparation and General Properties. Nitrosyl Complex (1). The diamagnetic nitrosyl complex was obtained in a good yield when nitrogen monoxide was introduced into an acetonitrile solution of $[CoPb(L)(CH_3OH)(ClO_4)_2]$. The FAB mass spectrum showed a prominent ion peak at m/z 813 that corresponds to $\{CoPb(L)(NO)(ClO_4)\}^+$. The nitrosyl complex behaves as a 2 : 1 electrolyte in dmf (Λ_M: 153 S cm^2 mol^{-1}).[16] It is likely that the Co–NO bond is retained but the perchlorate groups are released in dmf. The visible spectrum in dmf shows a band maximum at 580 nm (ε: 290 M^{-1} cm^{-1}). This absorption is lacking in the spectrum of the precursor Co$^{\text{II}}$Pb$^{\text{II}}$ complex and suggests the involvement of Co^{3+} in the complex **1**. A very intense band at 390 nm (ε: 11200 M^{-1} cm^{-1}) is typical of azomethine linkage.[17] The IR spectrum of **1** is characterized by a vibration at 1680 cm^{-1} that is attributable to the ν(NO) mode of nitrosyl group. The vibration frequency falls in the range found for nitrosyl cobalt(III) complexes,[4c,4d] but it is worth nothing that the frequency is much higher than the ν(NO) frequency of [Co(salen)NO] (1624 cm^{-1}).[4a]

Nitro Complex (2). Introduction of dioxygen into a dmf solution of **1** at room temperature formed $[CoPb(NO_2)(dmf)_2(ClO_4)]ClO_4$ (**2**). The FAB mass spectrum of **2** shows a prominent ion peak at m/z 829 that corresponds to $\{CoPb(L)(NO_2)(ClO_4)\}^+$. The ν(N–O) vibration at 1680 cm^{-1} found for **1** is replaced with new vibrations at 1438, 1310, and 810 cm^{-1}, which are assigned to the $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, and δ(ONO) modes of nitro group,[5a,18] respectively. This complex behaves as a 2 : 1 electrolyte in dmf (Λ_M: 168 S cm^2 mol^{-1}). The visible spectrum of **2** is very similar to that of **1**, showing a band maximum at 580 nm (ε: 330 M^{-1} cm^{-1}). The π–π^* transition band of the azomethine linkage is seen at 390 nm (ε: 13500 M^{-1} cm^{-1}).

Crystal Structures. Nitrosyl Complex (1). An ORTEP[19] view of the cationic part of **1** with 30% probability thermal ellipsoids is given in Fig. 1 together with the atom numbering scheme. The relevant bond distances and angles are given in Table 2.

The X-ray crystallography has proved that the complex cation consists of the macrocycle, one Co and one Pb ion, one nitrosyl group, two dmf molecules, and one perchlorate ion. The remaining perchlorate ion is free from coordination and captured in the crystal lattice. The Co ion resides in the "salen" site and the Pb ion in the "saldiene" site. The Co–Pb intermetallic separation bridged by the phenolic oxygens O(1) and O(2) is 3.511(2) Å. A noticeable feature of this complex is the bridging function of a dmf molecule between the Co and Pb ions through its oxygen O(3); the Co–O(3) and O(3)–Pb bond distances are 2.14(1) and 3.072(8) Å, respectively.

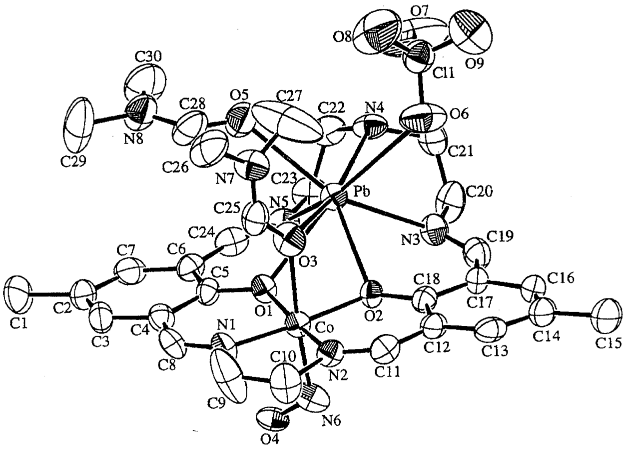


Fig. 1. ORTEP drawing of the $\{CoPb(L)(NO)(DMF)_2(ClO_4)\}^+$ part of **1** with the atom numbering scheme.

Table 2. Relevant Bond Distances (Å) and Angles (deg) of $[CoPb(L)(NO)(dmf)_2(ClO_4)]ClO_4$ (**1**)

	Distances		
Co–O(1)	1.913(7)	Co–O(2)	1.896(8)
Co–O(3)	2.14(1)	Co–N(1)	1.88(1)
Co–N(2)	1.88(1)	Co–N(6)	1.92(1)
Pb–O(1)	2.618(8)	Pb–O(2)	2.628(8)
Pb–O(3)	3.072(8)	Pb–O(5)	2.72(1)
Pb–O(6)	3.03(1)	Pb–N(3)	2.53(1)
Pb–N(4)	2.59(1)	Pb–N(5)	2.48(1)
N(6)–O(4)	1.14(2)	N(6)–O(4′)	1.13(2)
Co- - -Pb	3.511(2)		
	Angles		
O(1)–Co–O(2)	84.8(3)	O(1)–Co–O(3)	86.1(4)
O(1)–Co–N(1)	94.9(4)	O(1)–Co–N(2)	175.6(4)
O(1)–Co–N(6)	93.0(5)	O(2)–Co–O(3)	84.1(3)
O(2)–Co–N(1)	175.6(4)	O(2)–Co–N(2)	95.0(4)
O(2)–Co–N(6)	90.3(5)	O(3)–Co–N(1)	91.5(4)
O(3)–Co–N(2)	89.5(4)	O(3)–Co–N(6)	174.4(5)
N(1)–Co–N(2)	85.0(5)	N(1)–Co–N(6)	94.1(5)
N(2)–Co–N(6)	91.4(5)	O(1)–Pb–O(2)	58.6(2)
O(1)–Pb–O(3)	57.6(2)	O(1)–Pb–O(5)	93.2(3)
O(1)–Pb–O(6)	143.3(3)	O(1)–Pb–N(3)	109.7(3)
O(1)–Pb–N(4)	138.4(2)	O(1)–Pb–N(5)	69.3(3)
O(2)–Pb–O(3)	56.1(2)	O(2)–Pb–O(5)	144.6(3)
O(2)–Pb–O(6)	93.5(3)	O(2)–Pb–N(3)	68.9(3)
O(2)–Pb–N(4)	137.3(3)	O(2)–Pb–N(5)	109.9(3)
O(3)–Pb–O(5)	91.8(3)	O(3)–Pb–O(6)	87.7(3)
O(3)–Pb–N(3)	121.4(3)	O(3)–Pb–N(4)	160.5(3)
O(3)–Pb–N(5)	124.1(3)	O(5)–Pb–O(6)	100.2(4)
O(5)–Pb–N(3)	146.1(3)	O(5)–Pb–N(4)	77.7(4)
O(5)–Pb–N(5)	73.9(3)	O(6)–Pb–N(3)	76.5(4)
O(6)–Pb–N(4)	78.2(4)	O(6)–Pb–N(5)	147.3(3)
N(3)–Pb–N(4)	68.5(4)	N(3)–Pb–N(5)	90.8(4)
N(4)–Pb–N(5)	69.2(4)	Co–O(1)–Pb	100.5(3)
Co–O(2)–Pb	100.6(3)	Co–O(3)–Pb	82.6(3)
Co–N(6)–O(4)	117(1)	Co–N(6)–O(4′)	120(1)

The geometry about the Co is pseudo octahedral, with N(1), N(2), O(1), and O(2) of the macrocycle on the equatorial plane and the nitrosyl nitrogen N(6) and the bridging dmf oxygen O(3) at the axial positions. The sum of the in-plane angles O(1)–Co–O(2), O(1)–Co–N(1), N(1)–Co–N(2), O(2)–Co–N(2), and O(1)–Co–O(2) is 359.5°, and the O(3)–Co–N(6) angle is 174.4(4)°. The in-plane Co–N and Co–O bond distances fall in the range of 1.873(9)—1.911(7) Å which are compared to those of the precursor

$\mathrm{Co^{II}Pb^{II}}$ complex[8c)] and analogous $\mathrm{Co^{II}M^{II}}$ (M = Mn, Fe, Co) coomplexes,[8d)] in spite of different oxidation state of the Co ion. The axial Co–O(3) (2.136(9) Å) and Co–N(6) (1.92(1) Å) distances of **1**, on the other hand, are considerably shorter than those of the $\mathrm{Co^{II}M^{II}}$ complexes, in accord with 3+ oxidation state of the cobalt ion.

It must be mentioned that the Co–N(6)(nitrosyl) bond (1.92(1) Å) is slightly elongated relative to that of [Co(salen)NO] (1.809(4) Å). The nitrosyl N(6)–O(4) distance (1.14(2) Å) is also longer than that of [Co(salen)NO] (1.071(4) Å). This fact is not in harmony with the high ν(NO) frequency of **1**. It must be pointed out that the geometry around the Co is square-pyramidal for [Co(salen)NO] but is pseudo-octahedral for **1**. The elongation in the Co–N and N–O bonds in **1** may be ascribed to the trans effect of the strongly coordinated (bridging) dmf oxygen. The nitrosyl group has a bending mode with the Co–N(6)–O(4) angle of 120.0(1)° that is smaller than that of [Co(salen)NO] (128.0(3)°). The nitrosyl oxygen O(4) has disorder and is oriented along the O(1)–O(2) edge.

The Pb in the "saldien" site cannot reside within the cavity and has an eight-coordinate geometry together with two dmf oxygens (one bridging and one terminal) and one perchlorate oxygen. The Pb–N and Pb–O bond distances fall in the range of 2.49(1)—3.076(8) Å which are compared to those of $\mathrm{M^{II}Pb^{II}}$ complexes (M = Cu, Co).[8a,8c)]

The basal donor atoms O(1), O(2), N(1), and N(2) of the "salen" site form a good coplane; the deviations of the atoms from the least-squares plane are less than 0.002 Å. The donor atoms O(1), O(2), N(3), and N(5) of the "saldien" site also form a coplane; the deviations of the atoms from the least-squares plane are less than 0.0054Å. The two coplanes are bent at O(1)–O(2) edge with a dihedral angle of 2.32°. The Co in the "salen" site is 0.07 Å deviated from the basal least-squares plane towards N(6). The "Co(salen)"entity has a bow distortion; the dihedral angle defined by the two aromatic rings is 4.13°.

The O(3), N(7), C(25), C(26), and C(27) atoms of the dmf molecule reside on a plane and align along the Co–Pb–N(4) line. However, the complex cation has no symmetry as judged from its space group. When a least-squares plane is defined by Co, Pb, O(3), N(4), and N(6) (deviations of the atoms < 0.078 Å), the deviations of the dmf atoms from the least-squares plane are as follows: N(7) 0.3953, C(25) 0.4301, C(26) 0.9619, C(27) −0.1681 Å.

It must be mentioned that the bridging and the terminal dmf molecules significantly differ in bond distance. That is, the C(25)–O(3) formyl bond in the bridging dmf (1.24(2) Å) is elongated relative to the corresponding C(28)–O(6) bond in the terminal dmf (1.19(2) Å). Instead, the C(25)–N(7) bond distance in the bridging dmf (1.27(2) Å) is shortened relative to the corresponding C(28)–N(8) bond in the terminal dmf (1.34(2) Å).

Nitro Complex (2). An ORTEP drawing of the cationic part of **2** with 30% probability thermal ellipsoids is given in Fig. 2 together with the atom numbering scheme. The relevant bond distances and angles are given in Table 3.

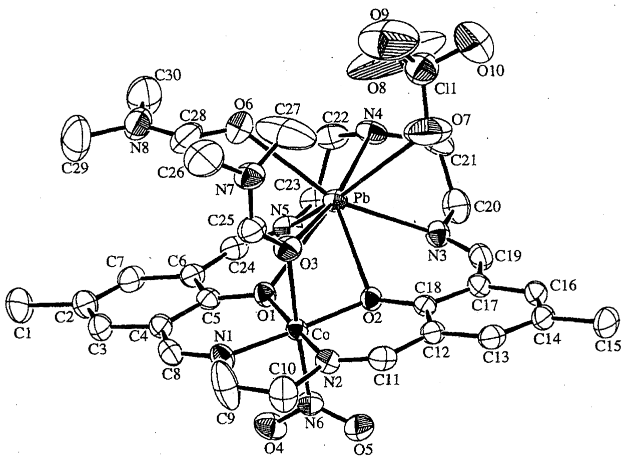


Fig. 2. ORTEP drawing of the $\{\mathrm{CoPb(L)(NO_2)(DMF)_2(ClO_4)}\}^+$ part of **2** with the atom numbering scheme.

Table 3. Relevant Bond Distances (Å) and Angles (deg) of $\mathrm{[CoPb(L)(NO_2)(dmf)_2(ClO_4)]ClO_4}$ (**2**)

	Distances		
Co–O(1)	1.900(4)	Co–O(2)	1.904(4)
Co–O(3)	2.011(5)	Co–N(1)	1.880(6)
Co–N(2)	1.866(6)	Co–N(6)	1.889(6)
Pb–O(1)	2.629(4)	Pb–O(2)	2.644(4)
Pb–O(3)	3.116(5)	Pb–O(6)	2.701(7)
Pb–O(7)	3.050(9)	Pb–N(3)	2.527(6)
Pb–N(4)	2.550(6)	Pb–N(5)	2.487(6)
N(6)–O(4)	1.221(8)	N(6)–O(5)	1.221(8)
Co- - -Pb	3.537(1)		
	Angles		
O(1)–Co–O(2)	84.1(2)	O(1)–Co–O(3)	86.9(2)
O(1)–Co–N(1)	95.5(2)	O(1)–Co–N(2)	177.5(2)
O(1)–Co–N(6)	91.2(2)	O(2)–Co–O(3)	84.9(2)
O(2)–Co–N(1)	178.0(2)	O(2)–Co–N(2)	95.8(2)
O(2)–Co–N(6)	90.7(2)	O(3)–Co–N(1)	93.2(3)
O(3)–Co–N(2)	90.6(2)	O(3)–Co–N(6)	175.3(2)
N(1)–Co–N(2)	84.5(3)	N(1)–Co–N(6)	91.3(3)
N(2)–Co–N(6)	91.3(3)	O(1)–Pb–O(2)	57.8(1)
O(1)–Pb–O(3)	55.1(1)	O(1)–Pb–O(6)	91.8(2)
O(1)–Pb–O(7)	138.7(2)	O(1)–Pb–N(3)	109.0(2)
O(1)–Pb–N(4)	138.7(2)	O(1)–Pb–N(5)	69.2(2)
O(2)–Pb–O(3)	53.9(1)	O(2)–Pb–O(6)	142.1(2)
O(2)–Pb–O(7)	88.7(2)	O(2)–Pb–N(3)	68.4(2)
O(2)–Pb–N(4)	137.9(2)	O(2)–Pb–N(5)	109.0(2)
O(3)–Pb–O(6)	91.2(2)	O(3)–Pb–O(7)	86.5(2)
O(3)–Pb–N(3)	119.4(2)	O(3)–Pb–N(4)	162.9(2)
O(3)–Pb–N(5)	122.2(2)	O(6)–Pb–O(7)	105.0(2)
O(6)–Pb–N(3)	149.0(2)	O(6)–Pb–N(4)	79.7(2)
O(6)–Pb–N(5)	75.1(2)	O(7)–Pb–N(3)	74.5(3)
O(7)–Pb–N(4)	82.1(3)	O(7)–Pb–N(5)	151.3(3)
N(3)–Pb–N(4)	69.5(2)	N(3)–Pb–N(5)	90.7(2)
N(4)–Pb–N(5)	69.6(2)	Co–O(1)–Pb	101.5(2)
Co–O(2)–Pb	100.9(2)	Co–O(3)–Pb	84.3(2)
Co–N(6)–O(4)	120.5(5)	Co–N(6)–O(5)	118.7(5)
O(4)–N(6)–O(5)	120.8(6)		

The X-ray crystallography has proved a dinuclear core very similar to that of **1**. The Co–Pb intermetallic separation triply bridged by the two phenolic oxygens O(1) and O(2) and a dmf oxygen O(3) is 3.537(1) Å. The Co assumes a pseudo octahedral geometry with the N_2O_2 donor atoms of the "salen" on the basal plane and the bridging dmf oxygen O(3) and the nitro nitrogen N(6) at the axial sites. The basal plane defined by O(1), O(2), N(1), and N(2) form a good coplane with very small deviations of the atoms ($<$ 0.0066 Å). The basal Co-to-ligand bond distances are compared to those of the nitrosyl complex **1**, whereas the axial Co–O(3) bond (2.011(5) Å) is shortened relative to that of **1**. The Co–N(6) (nitro) bond distance is 1.889(6) Å; which is shorter than the Co–N (nitrosyl) bond distance of **1**. The N(6)–O(4) and N(6)–O(5) bond distances of the nitro group are both 1.221(8) Å, a value which is common for the nitro complexes.[20] The Co is 0.04 Å deviated from the basal least-squares plane towards the nitro nitrogen. The plane defined by N(6), O(4), and O(5) of the nitro group aligns along the O(1)–O(2) edge. The O(3)–Co–N(6) angle is 175.3(2)°.

The geometry about the Pb resembles that of **1** and has an eight-coordinate geometry together with two dmf oxygens (one bridging and one terminal) and one perchlorate oxygen. The Pb–O(3) bond distance is 3.116(5) Å. The Pb-to-ligand bond distances are compared to those of the nitrosyl complex **1**.

The basal plane of the "salen" site and the plane defined by O(1), O(2), N(3), and N(5) of the "saldien" site are nearly coplanar in the nitro complex: the dihedral angle between the two least-squares planes is only 0.85°. A bow distortion is seen in the "Co(salen)" moiety; the dihedral angle defined by the two aromatic rings is 4.48°. The atoms of the bridging dmf molecule reside on a plane and align along Co–Pb line. However, the complex cation of **2** has no symmetry as in the case of **1**. When a least-squares plane is defined by Co, Pb, O(3), N(4), and N(6) (deviations of the atoms $<$ 0.035 Å), the deviations of the dmf atoms from the least-squares plane are as follows: N(7) 0.3724, C(25) 0.4463, C(26) 0.9972, C(27) −0.1987 Å.

Unexpectedly, the formyl C(25)–O(3) bond in the bridging dmf is 1.196(9) Å that is significantly short relative to the corresponding bond of the nitrosyl complex **1** (1.24(2) Å) and compared to the formyl C–O bond of terminal dmf.

Solution Structures. The solution structures of **1** and **2** have been studied by means of ^{1}H NMR, ^{13}C NMR, and ^{13}C–^{1}H COSY spectroscopies. The ^{1}H NMR spectrum of **1** in d_7-dmf is given in Fig. 3. The assignments of proton resonances for **1** are summarized in Table 4. The formyl proton resonance of the dmf molecules is observed as a singlet at 8.034 (m, m′) ppm. On the other hand, the methyl proton resonance of the dmf molecules is observed as two pairs of singlets at 2.957 (n) and 2.955 (n′) ppm and at 2.784 (o) and 2.782 (o′) ppm. This facts clearly indicate that the dmf molecules exist in two different environments in solution. We have confirmed that the dmf molecule bound to the Pb ion of the $\mathrm{Co^{II}Pb^{II}}$ complex $[\mathrm{CoPb(L)(dmf)_2(ClO_4)}]\mathrm{ClO_4}$ is exchanged with bulk dmf molecules faster than the time scale of NMR spectroscopy.[21] It is plausible that the Co–O(dmf)–Pb bridge of **1** is retained but the terminal dmf coordinated to the Pb ion is exchanged in d_7-dmf.

The NMR spectral feature of **1** (Fig. 3) is C_s symmetric

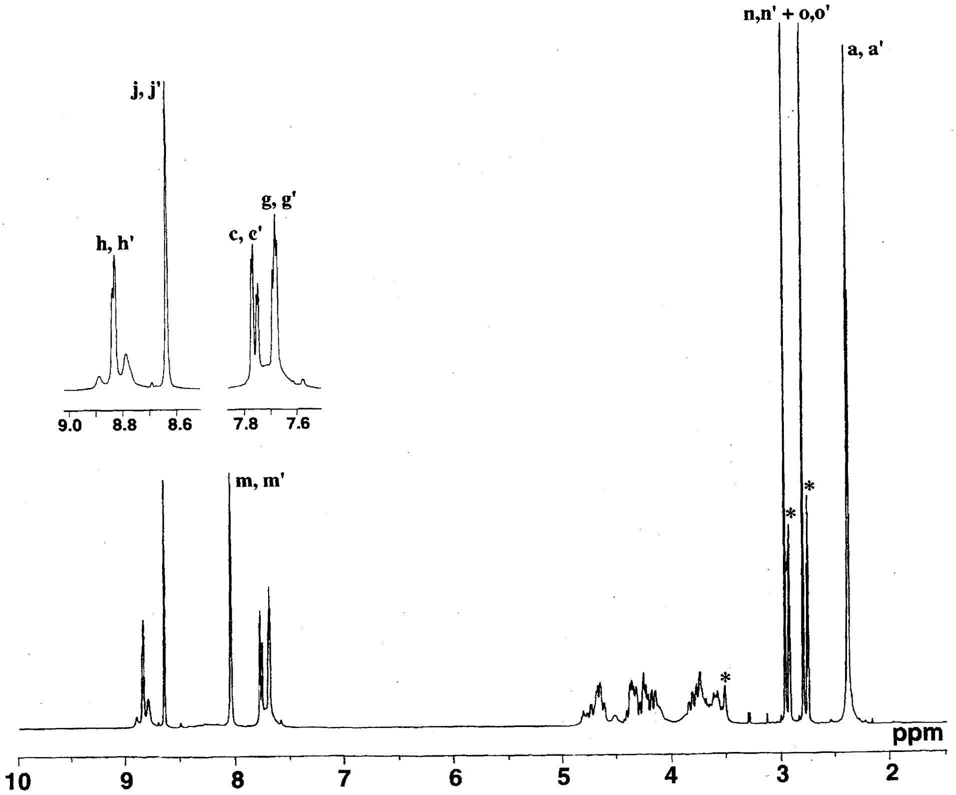
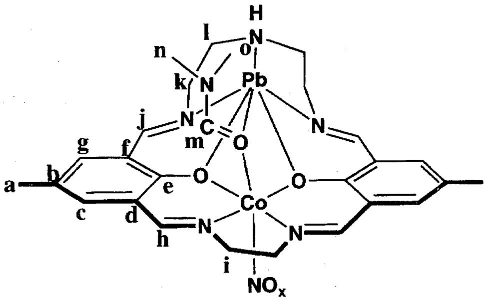


Fig. 3. ^{1}H NMR spectrum of **1** in d_7-dmf. The insert indicates the expansion of 7.5—9.0 ppm region.

Table 4. ^{1}H and ^{13}C NMR Spectral Data for **1** and **2**



		1	2
^{1}H NMR	a, a′	2.38, 2.37	2.37, 2.36
(δ/ppm)	c, c′	7.77, 7.75	7.76, 7.75
	g, g′	7.69, 7.67	7.68, 7.67
	h, h′	8.83, 8.82	8.83, 8.82
	j, j′	8.63	8.64
^{13}C NMR	a, a′	19.4, 19.3	19.4, 19.3
(δ/ppm)	b, b′	122.5, 122.2	122.5, 122.2
	c, c′	142.0, 141.9	141.9
	d, d′	126.6, 126.3	126.6, 126.4
	e, e′	160.5, 159.9	160.6, 160.0
	f, f′	126.2, 125.8	126.2, 125.8
	g, g′	145.1, 145.0	145.1, 145.0
	h, h′	171.7, 171.5	171.7, 171.5
	i, i′	67.7, 67.6	67.8, 67.7
	j, j′	170.0, 168.9	170.0, 169.0
	k, k′	59.6	59.6
	l, l′	54.5, 54.3	54.5, 54.3

at the first glance, but it becomes apparent from careful examination of the ^{1}H NMR spectrum that the complex has no symmetry with respect to the macrocyclic ligand. That is, seven resonances attributable to the azomethine and ring protons are seen in the region of 7.5—9.0 ppm (see the insert). The unsymmetric nature of the complex core in solution is also supported by ^{13}C NMR spectrum in d_7-dmf (Fig. 4, Table 4) that shows 24 independent carbon resonances for the macrocycle. The assignments of the azomethine and ring proton resonances have been made by ^{13}C–^{1}H COSY spectroscopy. The azomethine proton resonance of the "salen" site appears as two singlets at 8.83 (h) and 8.82 (h′) ppm and that of the "saldien" site as singlet at 8.63 (j, j′) ppm. Similarly, the resonance of the ring proton adjacent to the iminomethyl group of the "salen" appears as two doublets at 7.77 (c) and 7.75 (c′) ppm and that of the ring proton adjacent to the iminomethyl group of the "saldien" as two doublets at 7.69 (g) and 7.67 (g′) ppm. The methyl proton resonance of the aromatic ring is also observed as two singlets at 2.38 (a) and 2.37 (a′) ppm.

The NMR spectral feature of **2** is also unsymmetric with respect to the macrocycle L^{2-}. The assignments of proton and carbon resonances for the macrocycle are included in Table 4 for comparison.

From the above discussion it is evident that the Co–O-(dmf)–Pb bridge found for the nitrosyl **1** and the nitro **2** complexes is retained in dmf solution and this bridge gives rise to the unsymmetry of the dinuclear core.

Mechanism for Oxidative Conversion. It is known that nitrosyl cobalt complexes of quadridentate Schiff bases are air-oxidized to nitro or nitrato complexes in the presence of a Lewis base such as pyridine,[5] and a mechanistic scheme for the oxidative conversion is proposed.[1,5] Dioxygen may attack the nitrosyl nitrogen to form an intermediate with NO$_3$ group in peroxo structure (Co–N(O)O$_2$). This intermediate then reacts with another nitrosyl complex to give a dimer

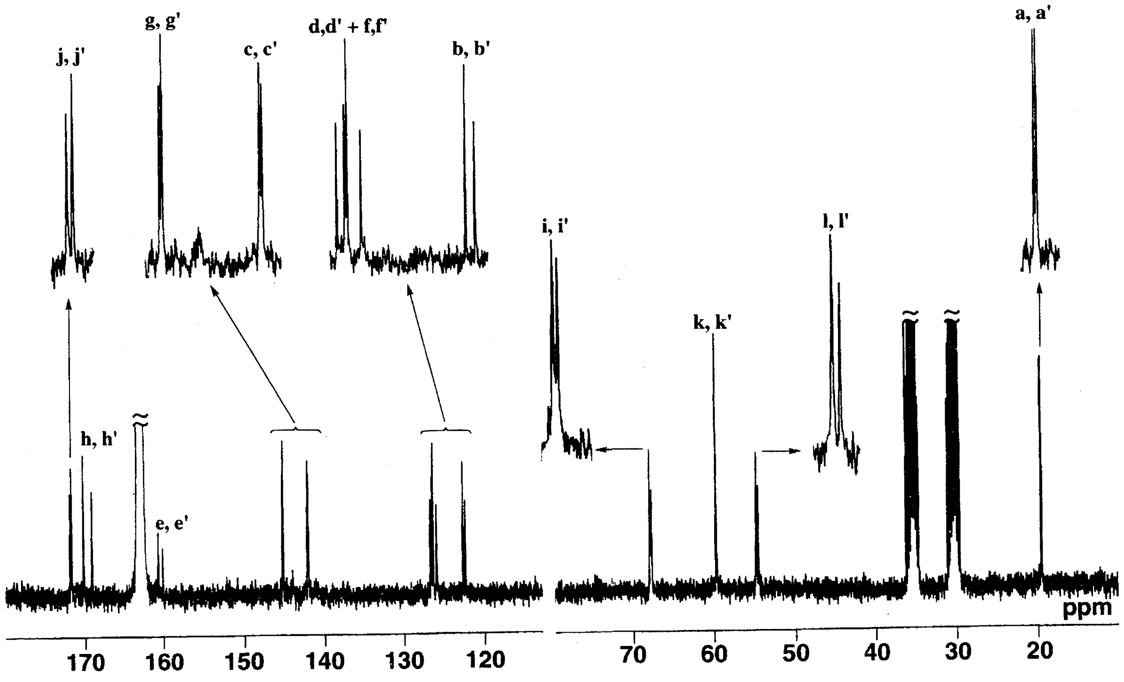


Fig. 4. ^{13}C NMR spectrum of **1** in d_7-dmf.

with unstable N–O–O–N linkage (Co–N(O)–O–O–(O)N–Co) and the O–O bond cleavage gives the final nitro complex. Nitrato complex may be formed by the isomerization of the intermediate with NO_3 in peroxo structure,[1,5] but no evidence was obtained for nitrato complex formation in this study. The function of a Lewis base is considered to make the NO nitrogen more nucleophilic through the coordination to the cobalt, at the trans position to the NO group. In the present case the oxidative conversion of the nitrosyl complex **1** to the nitro complex **2** occurred in the absence of a Lewis base, even in acetonitrile. This is understandable by that the bridging dmf oxygen serves as a Lewis base. So far such a dmf bridge has been confirmed only for the CoPb complexes with L^{2-}. The dmf bridge in the two complexes presumably arises from a high affinity of Pb^{2+} ion toward an oxygenic donor and the geometric feature of the CoPb core having an intermetallic Co–Pb separation corresponding to the Co–O–Pb bridge. Thus, the present study illustrates a neighboring effect of the adjacent Pb ion upon the reactivity at "Co(salen)" center.

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