DALTON
FULL PAPER

$Fe^{II}Pb^{II}$ and Fe^{III} complexes of macrocyclic compartmental ligands: different cyclization in stepwise template synthesis using Fe^{II}/Pb^{II} or Fe^{III}/Pb^{II} pairs

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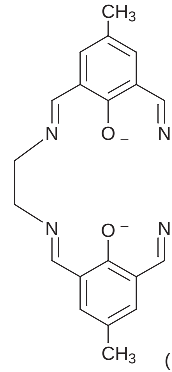
The reaction of [bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(II) with diethylenetriamine (dien) in the presence of Pb^{II} followed by the addition of NaNCS formed a $Fe^{II}Pb^{II}$ complex, $[FePb(L^1)(NCS)(dmf)(ClO_4)]$ **1**, where $(L^1)^{2-}$ is a dinucleating macrocyclic compartmental ligand derived from the [2 : 1 : 1] condensation of 2,6-diformyl-4-methylphenol, ethylenediamine and dien, having "salen"- and "saldien"-like metal-binding sites sharing the phenolic entities. The Fe resides in the "salen" site and the Pb in the "saldien" site: the Fe · · · Pb intermetallic separation is 3.438(2) Å. The Fe assumes a square-pyramidal geometry with an isothiocyanate nitrogen at the apex. The Pb has a seven-coordinate geometry with a dmf oxygen and a perchlorate oxygen at the axial sites. Complex **1** reacts with molecular dioxygen to give a μ-oxo complex $[\{FePb(L^1)(NCS)(dmf)(ClO_4)\}_2(O)]$. A similar reaction of chloro[bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(III) with dien in the presence of Pb^{II} formed a mononuclear Fe^{III} complex $[Fe(H_2L^2)(NCS)][ClO_4]_2{\cdot}dmf$ **2**, where H_2L^2 is a macrocycle derived from the [2 : 2] condensation of 2,6-diformyl-4-methylphenol and dien. The Fe resides in one "saldien" site and assumes an octahedral geometry with an isothiocyanate nitrogen in one apical position. Another metal-binding site formed with dien shows unusual condensation; one primary amino group of the dien condenses with one formyl group to form an usual C=N linkage and the remaining primary and secondary amino groups of the dien condense with another formyl group to form a five-membered imidazoline ring.

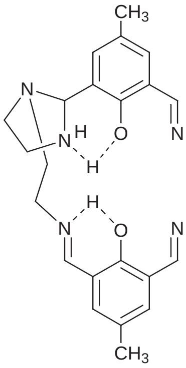
Introduction

It is well known that dinuclear cores exist at the active sites of many metalloenzymes and play an essential role in biological systems.[1] Recently, heterodinuclear FeM cores were recognized at metallobiosites of purple acid phosphatase (FeZn),[2] human calcineurin (FeZn),[3] human protein phosphatase 1 (FeMn)[4] and cytochrome c oxidase (FeCu)[5] and these findings have stimulated interest in the cooperative functions of dissimilar metal ions in heterodinuclear metal systems. It is believed that biological systems employ such heterodinuclear cores to achieve a specific function by the conjunction of the distinct roles played by the two metal ions.

In order to provide discrete heterodinuclear core complexes, we have developed unsymmetric compartmental ligands whose metal binding sites are not equivalent with respect to the cavity size, the coordination number, or the nature of the donor atoms.[6] The macrocyclic compartmental ligand $(L^1)^{2-}$ shown below, having "salen" [H_2salen = bis(salicylidene)ethylenediamine] and "saldien" [H_2saldien = bis(salicylidene)diethylenetriamine] entities sharing the phenolic moieties, is such a dinucleating compartmental ligand capable of providing discrete $M_a^{II}M_b^{II}$ core complexes having M_a^{II} in the "salen" site and M_b^{II} in the "saldien" site. So far $Cu^{II}M^{II}$, $Ni^{II}M^{II}$, $Co^{II}M^{II}$ and $Zn^{II}M^{II}$ (M = Pb, Mn, Fe, Co, *etc.*) complexes of this ligand have been reported.[7–13] Because of the importance of the FeM cores in metallobiosites as mentioned above, we aimed to synthesize $Fe^{II}Pb^{II}$ and $Fe^{III}Pb^{II}$ complexes of $(L^1)^{2-}$, as precursors for $Fe^{II}M^{II}$ and $Fe^{III}M^{II}$ complexes.



$(L^1)^{2-}$



H_2L^2

In this study we have noticed that a stepwise template reaction of [bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(II) with diethylenetriamine (dien) in the presence of Pb^{II} forms the desired $Fe^{II}Pb^{II}$ complex of $(L^1)^{2-}$, whereas a similar reaction of chloro[bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(III) with dien in the presence of Pb^{II} forms a different macrocycle (H_2L^2) as part of a mononuclear Fe^{III} complex. X-Ray structural characterization of the $Fe^{II}Pb^{II}$ and Fe^{III} complexes are reported together with their physicochemical properties.

Experimental

Measurements

Elemental C, H, N analyses were obtained from the Service

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Center of Elemental Analysis at Kyushu University. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer using KBr discs. Electronic spectra were measured in dmf on a Shimadzu UV-3100PC spectrophotometer at 25 °C. Molar conductances were measured in dmf on a DKK AOL-10 conductivity meter at 25 °C. Magnetic susceptibilities were determined on a Faraday balance in the temperature range 80–300 K (applied field 5000 G) and on a HOXAN HSM-D SQUID susceptometer in the range 1.9–80 K (applied field 500 G). Calibrations[14] were made with $Mn(NH_4)(SO_4)_2 \cdot 6H_2O$ for the SQUID susceptometer and with $[Ni(en)_3]S_2O_3$ (en = ethane-1,2-diamine) for the Faraday balance. Diamagnetic corrections for the constituent atoms were made using Pascal's constants.[15]

Preparations

2,6-Diformyl-4-methylphenol was prepared by a modification of the literature method.[16] Bis(3-formyl-5-methylsalicylidene)-ethylenediamine and its mononuclear iron(II) or iron(III) complexes were obtained by the literature methods.[17] All the operations for the synthesis of **1** were carried out in a nitrogen atmosphere using a glove box from the Vacuum Atmospheres Company model MO-40-IV or in an argon atmosphere using standard Schlenk apparatus. Unless otherwise stated all chemicals were purchased from commercial sources and used without further purification. Solvents were purified and dried by standard methods.

[FePb(L¹)(NCS)(dmf)(ClO₄)] 1. A solution of [bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(II) (0.50 g, 1.23 mmol) in methanol (20 cm³) and a solution of $Pb(ClO_4)_2 \cdot 3H_2O$ (0.566 g, 1.23 mmol) in methanol (10 cm³) were mixed and stirred at ambient temperature for 30 min. A methanol solution (10 cm³) of diethylenetriamine (0.127 g, 1.23 mmol) was added dropwise over the course of 20 min, and the mixture was refluxed for 1 h. Then a methanol solution (2 cm³) of NaNCS (0.10 g, 1.23 mmol) was added, and the mixture was stirred to give a black precipitate. Crystallization from a dmf–propan-2-ol mixture formed red crystals of **1** suitable for X-ray crystallography. The yield was 0.80 g (71%) (Calc. for $C_{28}H_{34}ClFeN_7O_7PbS$: C, 36.91; H, 3.76; N, 10.76. Found: C, 37.23; H, 3.92; N, 10.66%). μ_{eff} per Fe: 5.06 μ_B at 300 K. Selected IR data [ν/cm^{-1}] using KBr discs: 3320, 2930, 2850, 2040, 1640, 1140, 1110, 1080. Molar conductance [Λ_M/S cm^2 mol^{-1}] in dmf: 80. UV-vis data [λ/nm (ε/M^{-1} cm^{-1})] in dmf: 378 (16260), 512 (1870).

[{FePb(L¹)(NCS)(dmf)(ClO₄)}₂(O)] oxy-1. The complex **1** (0.50 g, 55 mmol) was dissolved in dmf (10 cm³) and molecular dioxygen was bubbled into the solution for 10 min at room temperature. The mixture was layered with propan-2-ol to form orange microcrystals. The yield was 0.43 g (85%) (Calc. for $C_{56}H_{68}Cl_2Fe_2N_{14}O_{15}Pb_2S_2$: C, 36.59; H, 3.73; N, 10.67. Found: C, 36.28; H, 3.81; N, 10.76%). Selected IR data [ν/cm^{-1}] using KBr discs: 3320, 2910, 2850, 2050, 1640, 1140, 1105, 1085, 845. Molar conductance [Λ_M/S cm^2 mol^{-1}] in dmf: 170. UV-vis data [λ/nm (ε/M^{-1} cm^{-1})] in dmf: 367 (24000), 410 (sh).

[Fe(H₂L²)(NCS)][ClO₄]₂·dmf 2. A solution of chloro[bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(III) (0.884 g, 2.0 mmol) in methanol (20 cm³) and a solution of $Pb(ClO_4)_2 \cdot 3H_2O$ (1.842 g, 4.00 mmol) in methanol (10 cm³) were mixed and stirred at ambient temperature for 30 min. A methanol solution (10 cm³) of diethylenetriamine (0.207 g, 2.0 mmol) was added dropwise over the course of 20 min, the mixture was stirred for 10 min, and resulting $PbCl_2$ was separated by suction filtration. Then a methanol solution (2 cm³) of NaNCS (0.163 g, 2.0 mmol) was added to the filtrate, and the mixture was refluxed for 1 h to give a black precipitate. Crystallization from a dmf–propan-2-ol mixture formed dark red crystals of **2** suitable for X-ray crystallography. The yield was 0.20 g (24%) (Calc. for $C_{30}H_{39}Cl_2FeN_8O_{11}S$: C, 42.57; H, 4.64; N, 13.24. Found: C, 42.64; H, 4.91; N, 13.34%). μ_{eff} per Fe: 5.85 μ_B at 300 K. Selected IR data [ν/cm^{-1}] using KBr discs: 3260, 3100, 2920, 2060, 1660, 1630, 1100. Molar conductance [Λ_M/S cm^2 mol^{-1}] in dmf: 121. UV-vis data [λ/nm (ε/M^{-1} cm^{-1})] in dmf: 338 (8540), 394 (9620), 440 (sh), 510 (4380).

Table 1 Crystallographic data for [FePb(L¹)(NCS)(dmf)(ClO₄)] **1** and [Fe(H₂L²)(NCS)][ClO₄]₂·dmf **2**

	1	**2**
Formula	$C_{28}H_{34}ClFeN_7O_7PbS$	$C_{30}H_{41}Cl_2FeN_8O_{11}S$
M	911.18	848.51
Crystal color	Red	Dark red
Crystal size/mm	0.2 × 0.2 × 1.00	0.5 × 0.5 × 0.5
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*P*2₁/*c*
a/Å	20.064(7)	9.892(3)
b/Å	21.306(8)	24.786(7)
c/Å	15.751(4)	15.500(4)
β/°		95.38(2)
U/Å³	6733(3)	3783(1)
Z	8	4
D_c/g cm^{-3}	1.798	1.489
λ(Mo-Kα)/Å	0.71069	0.71069
No. of reflections	6544	7257
R	0.040	0.062
R_w	0.057	0.104

X-Ray crystallography

A single crystal of **1** was enclosed in a capillary tube together with the mother-solution. A single crystal of **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 50.0° at a scan speed of 16.0° min^{-1} (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics. Crystal data and details of the structure determinations are summarized in Table 1. 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 θ/λ and various classes of indices showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber.[18] Anomalous dispersion effects were included in F_c;[19] the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[20] The values for the mass attenuation coefficients were those of Creagh and Hubbel.[21] All the calculations were performed on an IRIS Indigo computer using the TEXSAN crystallographic software package.[22]

CCDC reference number 186/1285.

See http://www.rsc.org/suppdata/dt/1999/367/ for crystallographic files in .cif format.

Results and discussion

[FePb(L¹)(NCS)(dmf)(ClO₄)] 1

In our previous studies the M^{II}Pb^{II} complexes (M = Cu, Ni, Co, Zn) of the macrocyclic ligand (L^1)$^{2-}$ were obtained by the template reaction of [bis(3-formyl-5-methylsalicylidene)ethylene-

Table 2 Relevant bond distances (Å) and angles (°) for [FePb(L^1)(NCS)(dmf)(ClO$_4$)] **1**

Fe–O(1)	2.011(8)	Fe–O(2)	2.009(8)
Fe–N(1)	2.095(10)	Fe–N(2)	2.104(10)
Fe–N(6)	2.013(9)	Pb–O(1)	2.656(8)
Pb–O(2)	2.606(8)	Pb–O(3)	2.386(8)
Pb–O(4)	3.10(2)	Pb–N(3)	2.59(1)
Pb–N(4)	2.54(1)	Pb–N(5)	2.62(1)
Fe···Pb	3.438(2)		
Fe–O(1)–Pb	93.9(3)	Fe–O(2)–Pb	95.4(3)
O(1)–Fe–O(2)	99.4(3)	O(1)–Fe–N(1)	86.7(4)
O(1)–Fe–N(2)	152.6(3)	O(1)–Fe–N(6)	102.0(3)
O(2)–Fe–N(1)	154.7(3)	O(2)–Fe–N(2)	85.7(4)
O(2)–Fe–N(6)	102.5(4)	N(1)–Fe–N(2)	78.3(4)
N(1)–Fe–N(6)	100.2(4)	N(2)–Fe–N(6)	103.2(4)
O(1)–Pb–O(2)	71.3(2)	O(1)–Pb–O(3)	76.8(3)
O(1)–Pb–O(4)	116.1(7)	O(1)–Pb–N(3)	137.3(3)
O(1)–Pb–N(4)	132.9(3)	O(1)–Pb–N(5)	68.8(3)
O(2)–Pb–O(3)	75.1(3)	O(2)–Pb–O(4)	142.2(4)
O(2)–Pb–N(3)	70.9(3)	O(2)–Pb–N(4)	134.9(3)
O(2)–Pb–N(5)	136.2(3)	O(3)–Pb–O(4)	141.9(4)
O(3)–Pb–N(3)	75.2(3)	O(3)–Pb–N(4)	76.0(3)
O(3)–Pb–N(5)	79.0(3)	O(4)–Pb–N(3)	105.8(7)
O(4)–Pb–N(4)	69.6(6)	O(4)–Pb–N(5)	73.9(5)
N(3)–Pb–N(4)	68.7(3)	N(3)–Pb–N(5)	134.3(3)
N(4)–Pb–N(5)	68.8(3)		

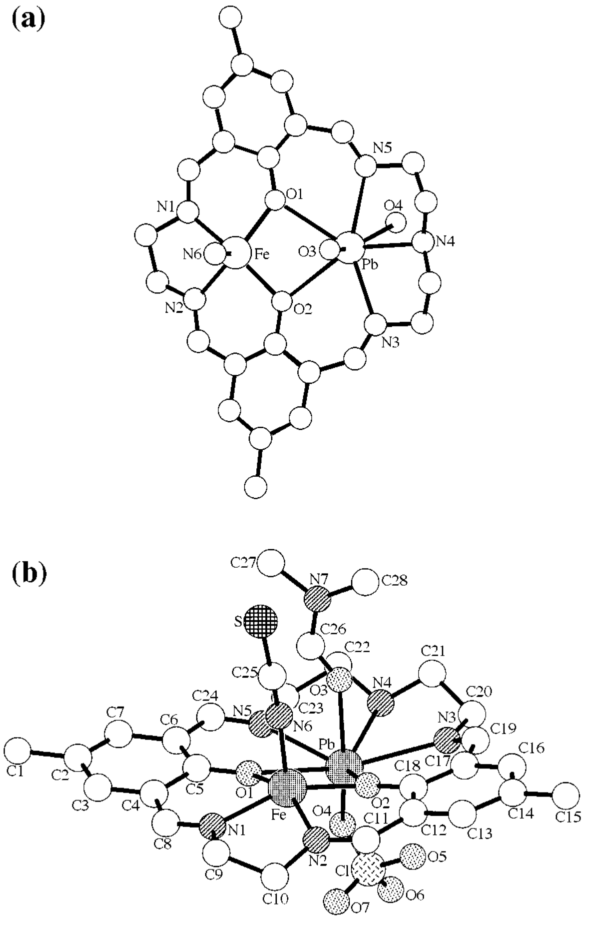


Fig. 1 Perspective views of the Fe^{II}Pb^{II} complex **1**: (a) top view and (b) side view.

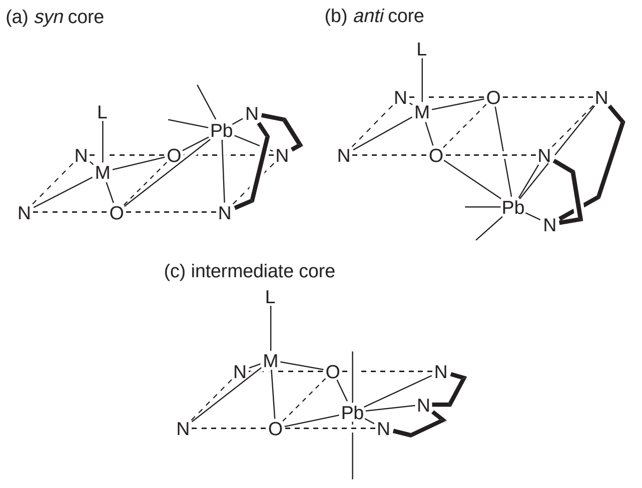
diaminato]metal(II) with dien in the presence of Pb^{II} ion.[7–12] The Fe^{II}Pb^{II} complex [FePb(L^1)(NCS)(dmf)(ClO$_4$)] **1** was prepared by a similar reaction between [bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(II) and dien in the presence of Pb^{II}, followed by the addition of an equimolar amount of NaNCS.

A perspective view of **1** is shown in Fig. 1 together with the atom-numbering scheme. The relevant bond distances and angles are given in Table 2.

Complex **1** has a dinuclear Fe^{II}Pb^{II} core bridged by the two phenolic oxygens O(1) and O(2) with a Fe···Pb intermetallic separation of 3.438(2) Å. The Fe resides in the "salen" site and assumes a square-pyramidal geometry with an isothiocyanate nitrogen N(6) at the axial site. The basal donor atoms O(1), O(2), N(1) and N(2) of the "salen" site form a near coplane; the deviations of the atoms from the least-squares plane are less than 0.04 Å. The Fe is deviated 0.42 Å from the basal least-squares plane towards the axial isothiocyanate nitrogen N(6). The basal Fe–N and Fe–O bond distances fall in the range 2.009(8)–2.104(10) Å which are common for high-spin Fe^{II}.[23] The axial Fe–N(6) distance [2.013(9) Å] is slightly shorter compared with the in-plane Fe–N(1) [2.095(10) Å] and Fe–N(2) [2.104(10) Å] distances.

The Pb ion in the "saldien" site has a seven-coordinate geometry with one dmf oxygen O(3) and one perchlorate oxygen O(4) at the axial sites. The donor atoms O(1), O(2), N(3), N(4) and N(5) of the "saldien" site reside on a near coplane; the deviations of the atoms from the least-squares plane are less than 0.04 Å and the sum of the bite angles O(1)–Pb–O(2), O(2)–Pb–N(3), N(3)–Pb–N(4), N(4)–Pb–N(5) and O(1)–Pb–N(5) is 348.5°. The axial O(3)–Pb–O(4) is extremely bent [141.9(4)°]. Thus, the geometry about Pb can be regarded as a distorted pentagonal-bipyramid with a dmf oxygen O(3) and a perchlorate oxygen O(4) at the axial sites. The in-plane Pb-to-ligand bond distances range from 2.54(1) to 2.656(8) Å. The axial Pb–O(3) (dmf) bond distance is very short [2.386(8) Å], to compensate for this, the axial Pb–O(4) (perchlorate) bond is significantly elongated [3.10(2) Å]. The Pb is deviated 0.61 Å from the least-squares plane towards O(4). If we neglect the long Pb–O(4) bond, the Pb has a rare umbrella-like shape. A similar umbrella-like shape about Pb is recognized for [ZnPb(L^1)(BNP)]ClO$_4$ [BNP$^-$ = bis(*p*-nitrophenyl)phosphate].[12] The basal least-squares plane of the "salen" site and that of the "saldien" site are bent at the O(1)···O(2) edge with a dihedral angle of 3.98°.

Two distinct core structures have been recognized for the M^{II}Pb^{II} complexes of (L^1)$^{2-}$ (see below). In one core, the Pb is largely displaced from the mean molecular plane, owing to the mismatch between the ionic radius of the Pb^{II} and the cavity size of the "saldien" site, and the axial ligand attached to M is situated *syn* with respect to the Pb atom [*syn* core (a)]. In another core, the axial ligand attached to M is situated *anti* with respect to the displaced Pb atom [*anti* core (b)]. The *syn* core is found for a Co^{II}Pb^{II} complex [CoPb(L^1)(CH$_3$OH)(ClO$_4$)$_2$][9] and a Co^{III}Pb^{II} complex [CoPb(L^1)(OH)(CH$_3$CN)$_2$]$^{2+}$,[24] and the *anti* core for a nitrosyl Co^{III}Pb^{II} complex [CoPb(L^1)(NO)(dmf)$_2$(ClO$_4$)]$^{+}$ [11] and a Zn^{II}Pb^{II} complex [ZnPb(L^1)(CH$_3$OH)(dmf)(ClO$_4$)]$^{+}$.[25]



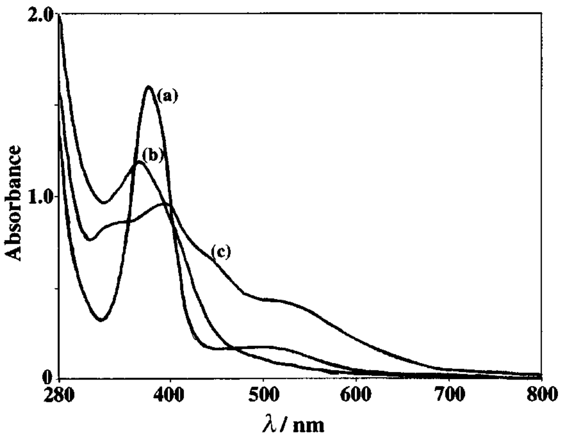


Fig. 2 Absorption spectra of **1** (a), oxy-**1** (b) and **2** (c) in dmf ($c \approx 1 \times 10^{-3}$ M for **1** and **2**; ≈0.5 × 10^{-3} M for oxy-**1**).

The core structure of **1** can be depicted as an intermediate between the *syn* and *anti* cores, indicating that the two cores can be interconverted through an intermediate core. A pentagonal arrangement of the Pb^{II} in the "saldien" site requires a considerably large O(1)···O(2) separation (3.069 Å) and thence a large O(1)–Pb–O(2) bite angle (≈71°). This necessitates a distortion in the $\{MN_2O_2\}$ environment resulting in the enlargement of the O(1)–M–O(2) bite angle (≈99°); an O(1)–M–O(2) angle of 85° is usually found for bis(phenoxo) bridged dinuclear complexes.[6] The *syn* and *anti* cores occur when the M in the "salen" site resides within the N_2O_2 cavity [small O(1)–M–O(2) angle] and thence the "saldien" site has little flexibility to accommodate large Pb^{II} within its N_3O_2 cavity [small O(1)–Pb–O(2) angle; ≈60°]. When the M in the "salen" site is largely displaced from the N_2O_2 least-squares plane [large O(1)–M–O(2) angle], the "saldien" site has considerable flexibility for accommodating Pb^{II} within its N_3O_2 cavity, providing the intermediate core.

Complex **1** shows the ν(CN) mode of the thiocyanate ion at 2040 cm^{-1} in agreement with its coordination through nitrogen.[26] The ν_3 mode of the perchlorate group is split into three bands (1140, 1110, 1080 cm^{-1}). The magnetic moment at room temperature is 5.06 μ_B comparable to the values found for Fe(salen)[27a] and Fe(salen)(py).[27b] The complex behaves as a 1 : 1 electrolyte in dmf (Λ_M 80 S cm^2 mol^{-1}).[28] It is likely that the Fe–NCS bond is retained but the perchlorate group is free from coordination in dmf. The visible spectrum of **1** in dmf shows an intense absorption band at 378 nm (ε 16260 M^{-1} cm^{-1}) and a moderately intense band at 512 nm (ε 1870 M^{-1} cm^{-1}) [Fig. 2(a)]. The former can be assigned to the π–π* transition of the azomethine linkage[29] and the latter band may be assigned to a charge transfer band associated with the Fe^{II} ion.

Complex **1** is air sensitive especially in solution. A dmf solution of **1** undergoes an immediate color change from red to yellow upon exposure to air, and orange microcrystals ($[\{FePb(L^1)(NCS)(dmf)(ClO_4)\}_2(O)]$ (oxy-**1**)) were deposited in good yield when propan-2-ol was diffused into the oxidized solution. The IR spectrum of oxy-**1** is very similar to that of **1**, except for a new strong band at 845 cm^{-1}. This IR band is characteristic of μ-oxo Fe^{III} complexes and can be assigned to the ν_{as}(Fe–O–Fe) mode.[30,31] The complex behaves as a 2 : 1 electrolyte in dmf (Λ_M 170 S cm^2 mol^{-1}). The electronic spectrum of oxy-**1** in dmf is shown in Fig. 2(b). It shows an absorption at 367 nm (ε 24000 M^{-1} cm^{-1}) together with a discernible shoulder near 400 nm. It is known that the absorption spectra of μ-oxodiiron(III) complexes exhibit charge transfer bands between oxygen and iron(III) in the range 300–400 nm.[31] Therefore, it is likely that the band at 367 nm is a superposition of the azomethine π–π* transition band and the charge transfer bands from oxygen to Fe^{III}. The shoulder near 400 nm can be assigned to the LMCT band from oxygen to Fe^{III}. No absorption in the visible region is in accord with the high-spin d^5 electronic configuration of the Fe^{III} ion.

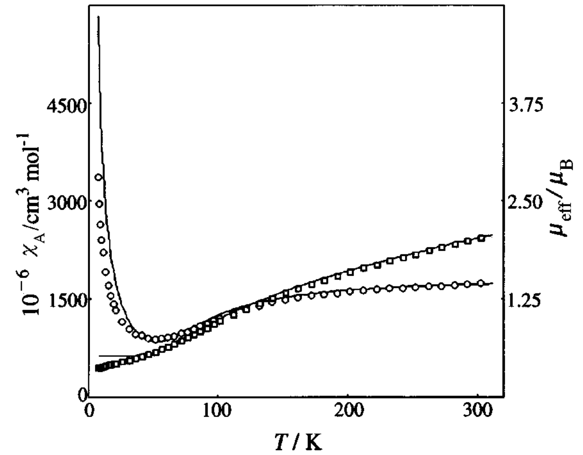


Fig. 3 μ_{eff} *vs.* T (□) and χ_A *vs.* T (○) plots for oxy-**1**.

The magnetic moment of oxy-**1** is subnormal at 300 K (2.91 μ_B per Fe). The magnetic susceptibility of oxy-**1** was measured in the temperature range 300–1.9 K; the plots of χ_A *vs.* T and μ_{eff} *vs.* T are given in Fig. 3.

Magnetic analysis has been made using the magnetic susceptibility expression [eqn. (1)] for the ($S_1 = 5/2$)–($S_2 = 5/2$) spin

$$\chi_A = \{Ng^2\beta^2/k(T-\theta)\}[\{55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)\}/\{11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)\}](1-\rho) + \{Ng^2\beta^2/k(T-\theta)\}(35/12)\rho + N\alpha \quad (1)$$

system based on the Heisenberg model, where ρ is the fraction for monometallic impurity and the other symbols have their usual meanings. Cryomagnetic data in the temperature range 50–300 K could be simulated by eqn. (1) using the magnetic parameters $J = -90.6$ cm^{-1}, $g = 2.0$, $N\alpha = 0$, $\theta = 0$ and $\rho = 0.39\%$, but the simulation in the range 1.9–50 K was incomplete. This fact suggests the operation of a secondary effect such as intramolecular interaction or zero-field splitting of the Fe^{III} ground state. Such a discrepancy below 50 K was always observed when simulations were carried out using a nonzero θ. It appears that the zero-field splitting of Fe^{III} operates as the secondary effect in oxy-**1**. Despite the unsatisfactory magnetic fitting in the temperature range 1.9–50 K, the cryomagnetic nature of oxy-**1** adds support for its μ-oxodiiron(III) core structure. The exchange integral ($J = -90.6$ cm^{-1}) observed is comparable with those of oxo-bridged diiron(III) complexes.[31]

$[Fe(H_2L^2)(NCS)][ClO_4]_2\cdot dmf$ 2

The reaction of chloro[bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(III) with dien in the presence of Pb^{II} ion, followed by the addition of NaNCS, resulted in the formation of a mononuclear Fe^{III} complex $[Fe(H_2L^2)(NCS)][ClO_4]_2\cdot dmf$ **2**, of a different macrocyclic ligand in a protonated form. Based on elemental analysis, the ligand H_2L^2 is supposed to be a [2 : 2] condensation product between 2,6-diformyl-4-methylphenol and dien. The result suggests the recombination of the proligand, bis(3-formyl-5-methylsalicylidene)ethylenediamine, with dien in the course of cyclization. This is proved by an X-ray crystallographic study of **2**. An ORTEP[32] drawing of the mononuclear Fe^{III} complex **2** is shown in Fig. 4 together with the atom-numbering scheme. The relevant bond distances and angles are given in Table 3.

X-Ray crystallography has proved that the complex consists of the macrocycle (H_2L^2), one Fe^{III} ion, one thiocyanate ion, one dmf molecule, and two perchlorate ions. The macrocycle H_2L^2 is constructed by the [2 : 2] condensation between 2,6-diformyl-4-methylphenol and dien. One site formed with dien provides the usual "saldien" site. The Fe resides in this site

Table 3 Relevant bond distances (Å) and angles (°) for $[Fe(H_2L^2)(NCS)][ClO_4]_2$·dmf **2**

Fe–O(1)	1.954(3)	Fe–O(2)	1.932(3)
Fe–N(1)	2.170(4)	Fe–N(2)	2.229(4)
Fe–N(3)	2.109(4)	Fe–N(7)	2.019(4)
O(1)–Fe(1)–O(2)	87.4(1)	O(1)–Fe(1)–N(1)	84.5(1)
O(1)–Fe(1)–N(2)	159.8(1)	O(1)–Fe(1)–N(3)	98.6(1)
O(1)–Fe(1)–N(7)	99.7(2)	O(2)–Fe(1)–N(1)	171.7(1)
O(2)–Fe(1)–N(2)	111.2(1)	O(2)–Fe(1)–N(3)	83.7(1)
O(2)–Fe(1)–N(7)	91.2(1)	N(1)–Fe(1)–N(2)	76.5(1)
N(1)–Fe(1)–N(3)	95.6(1)	N(1)–Fe(1)–N(7)	92.0(2)
N(2)–Fe(1)–N(3)	76.6(2)	N(2)–Fe(1)–N(7)	88.0(2)
N(3)–Fe(1)–N(7)	160.7(2)		

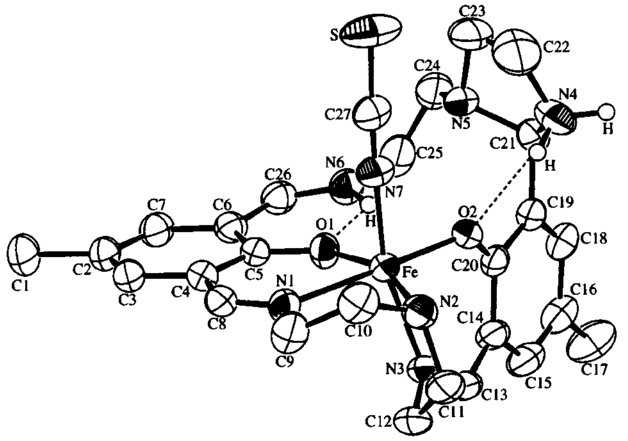


Fig. 4 An ORTEP view of the Fe^{III} complex **2**.

and assumes a six-coordinate geometry with an isothiocyanate nitrogen in one apical position. The geometry about the metal can be regarded as pseudo-octahedral with O(1), O(2), N(1) and N(2) on the basal plane and N(3) and N(7) at the axial sites. The N(3)–Fe–N(7) angle is 160.7(2)°. The Fe–O(1) and Fe–O(2) bond distances [1.954(3) and 1.932(3) Å] are fairly short compared with the Fe–N bond distances [2.019(4)–2.229(4) Å]. It should be mentioned that the Fe–N(7) (isothiocyanate) bond distance [2.019(4) Å] is significantly short relative to the other Fe–N (macrocycle) bond distances [2.109(4)–2.229(4) Å].

Another site formed with dien shows unusual condensation; one primary amino group of the dien condenses with one formyl group to form an usual C=N linkage and the remaining primary and secondary amino groups of the dien condense with another formyl group to form a five-membered imidazoline ring. The imidazoline nitrogen N(4) and the azomethine nitrogen N(6) are protonated, respectively, and hydrogen bonding exists between O(1) and N(6) and between O(2) and N(4).

Similar condensations between dicarbonyl compounds and polyamines to afford macrocycles containing five-membered imidazoline or six-membered pyrimidine rings have been reported.[33] Condensations between dicarbonyl compounds and hydroxy-containing amines to give macrocycles containing oxazoline rings are also known.[34] The origin for recombination of the proligand in the template reaction with dien to form complex **2** of the macrocycle H_2L^2 probably relates to the thermodynamic preference of this complex.

The IR spectrum of **2** is characterized by a ν(CN) stretching mode of the isothiocyanate group at 2060 cm^{-1}, a ν_{as}(N–H) vibration of the imidazoline ring at 3100 cm^{-1}, and two ν(C=N) vibration modes at 1660 and 1630 cm^{-1}. The former ν(C=N) mode is attributed to the N(6)–C(26) linkage free from coordination and the latter mode to the C=N linkages associated with the coordination to the Fe^{III}. The magnetic moment at room temperature is 5.85 μ_B, which is common for high spin Fe^{III} ($\mu_{S.O.} = 5.92\ \mu_B$). Complex **2** behaves as 1:2 electrolyte in dmf (Λ_M 121 S cm^2 mol^{-1}), indicating that the Fe–NCS bond is retained. This is in harmony with the short Fe–N(NCS) bond distance demonstrated by the X-ray crystallography. The visible spectrum of **2** in dmf [Fig. 2(c)] shows two intense absorption bands at 338 nm (ε 8540 M^{-1} cm^{-1}) and 394 nm (ε 9620 M^{-1} cm^{-1}). They can be assigned to the π–π^* transition of the azomethine groups: the former to the C=N group free from coordination and the latter to that associated with the coordination to Fe^{III}. The moderately intense bands at ≈440 nm (ε 4000 M^{-1} cm^{-1}) and 510 nm (ε 4380 M^{-1} cm^{-1}) may be assigned to charge-transfer bands from the phenolate oxygen to the Fe^{III} ion.[35]

Conclusion

The template reaction of [bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(II) with dien in the presence of Pb^{II} formed a $Fe^{II}Pb^{II}$ complex of the macrocycle $(L^1)^{2-}$, $[FePb(L^1)(NCS)(dmf)(ClO_4)]$ **1**, that may be used as a precursor for $Fe^{II}M^{II}$ complexes of $(L^1)^{2-}$. On the other hand, a similar template reaction of chloro[bis(3-formyl-5-methylsalicylidene)ethylenediaminato]iron(III) with dien in the presence of Pb^{II} formed a Fe^{III} complex of the macrocycle H_2L^2, $[Fe(H_2L^2)(NCS)][ClO_4]_2$·dmf **2**. In this reaction the recombination of the proligand, bis(3-formyl-5-methylsalicylidene)ethylenediamine, with dien occurred to form the unusual [2:2] condensation product between 2,6-diformyl-4-methylphenol and dien. Complex **1** was oxidized in dmf with molecular dioxygen to provide a μ-oxo dimer $[\{FePb(L^1)(NCS)(dmf)(ClO_4)\}_2(O)]$ oxy-**1** that could prove to be a promising precursor for $Fe^{III}M^{II}$ core complexes of $(L^1)^{2-}$.

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References

1 D. E. Fenton and H. Ōkawa, *Perspectives on Bioinorganic Chemistry*, JAI Press, London, 1993, vol. 2, p. 81; K. D. Karlin, *Science*, 1993, **261**, 701; Special thematic issue on “Metal-Dioxygen Complexes”, *Chem. Rev.*, 1994, **94**, 567–856; Special thematic issue on “Bioiorganic Enzymology”, *Chem. Rev.*, 1996, **96**, 2237–3042.

2 N. Strater, T. Klabunde, P. Tucker, H. Witzel and B. Krebs, *Science*, 1995, **268**, 1489.

3 C. R. Kissinger, H. E. Parge, D. R. Knighton, C. T. Lewis, L. A. Pelletier, A. Tempczyk, V. J. Kalish, K. D. Tucker, R. E. Showalter, E. W. Moomaw, L. N. Gastinel, N. Habuka, X. Chen, F. Maldonado, J. E. Barker, R. Bacquet and J. E. Villafranca, *Nature* (*London*), 1995, **378**, 641.

4 M.-P. Egloff, P. T. W. Cohen, P. Reinemer and D. Barford, *J. Mol. Biol.*, 1995, **254**, 942.

5 T. Tsukihara, H. Aoyama, E. Yamashita, T. Tomizaki, H. Yamaguchi, K. Shinzawa-Itoh, R. Nakashima, R. Yaono and S. Yoshikawa, *Science*, 1995, **269**, 1069; 1996, **272**, 1136; S. Iwata, C. Ostermeier, B. Ludwig and H. Michel, *Nature* (*London*), 1995, **376**, 660.

6 H. Ōkawa, H. Furutachi and D. E. Fenton, *Coord. Chem. Rev.*, 1998, **174**, 51 and refs. therein.

7 H. Ōkawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida and D. E. Fenton, *Inorg. Chem.*, 1993, **32**, 2949.

8 J. Nishio, H. Ōkawa, S. Ohtsuka and M. Tomono, *Inorg. Chim. Acta*, 1994, **218**, 27.

9 J. Shimoda, H. Furutachi, M. Yonemura, M. Ohba, N. Matsumoto and H. Ōkawa, *Chem. Lett.*, 1996, 979.

10 H. Furutachi and H. Ōkawa, *Inorg. Chem.*, 1997, **36**, 3911.

11 H. Furutachi and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 671.

12 M. Yamami, H. Furutachi, T. Yokoyama and H. Ōkawa, *Chem. Lett.*, 1998, 211.

13 H. Furutachi, S. Fujinami, M. Suzuki and H. Ōkawa, *Chem. Lett.*, 1998, 779.
14 N. F. Curtis, *J. Chem. Soc.*, 1961, 3147.
15 E. A. Boudreaux and L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, Wiley, New York, 1976, pp. 491–494.
16 D. A. Denton and H. Suschitzky, *J. Chem. Soc.*, 1963, 4741.
17 H. Ōkawa and S. Kida, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 751; H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759; Y. Nishida, S. Oshio and S. Kida, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 119.
18 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. IV, 1974.
19 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.
20 D. C. Creagh and W. J. McAuley, *International Tables for X-Ray Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, pp. 219–222.
21 D. C. Creagh and J. H. Hubbell, *International Tables for X-Ray Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, pp. 200–206.
22 TEXSAN, Molecular Structure Corporation, Houston, TX, 1985.
23 C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.
24 H. Furutachi and H. Ōkawa, unpublished work.
25 M. Yamami, H. Furutachi, T. Yokoyama and H. Ōkawa, *Inorg. Chem.*, in the press.
26 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 3rd edn., 1978, p. 270.
27 (*a*) A. Earnshaw, E. A. King and L. F. Larkworthy, *J. Chem. Soc. A*, 1968, 1048; (*b*) F. Calderazzo, C. Floriani, R. Henzi and F. L'Eplattenier, *J. Chem. Soc. A*, 1969, 1378.
28 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
29 B. Bosnich, *J. Am. Chem. Soc.*, 1968, **90**, 627.
30 J. Sanders, W. D. Wheeler, A. K. Shiemke, B. A. Averill and T. M. Loehr, *J. Am. Chem. Soc.*, 1989, **111**, 8084.
31 D. M. Kurtz, jun., *Chem. Rev.*, 1990, **90**, 585; L. Que, jun. and A. E. True, *Prog. Inorg. Chem.*, 1990, **38**, 97; R. C. Reem, J. M. McCormick, D. E. Richardson, F. J. Devlin, P. J. Stephens, R. L. Musselman and E. I. Solomon, *J. Am. Chem. Soc.*, 1989, **111**, 4688.
32 C. K. Johnson, ORTEP, Report 3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
33 S. Tamburini, P. A. Vigato, D. Chiarello and P. Traldi, *Inorg. Chim. Acta*, 1989, **156**, 271; M. G. B. Drew, J. Nelson and S. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678; R. Menif and A. E. Martell, *J. Chem. Soc., Chem. Commun.*, 1989, 1521; R. Menif, A. E. Martell, P. J. Squattrito and A. Clearfield, *Inorg. Chem.*, 1990, **29**, 4723; M. P. Ngwenya, D. Chen, A. E. Martell and J. Reibenspies, *Inorg. Chem.*, 1991, **30**, 2732; K. Motoda, H. Sakiyama, N. Matsumoto, H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1176.
34 H. Adams, N. A. Bailey, D. E. Fenton, R. J. Good, R. Moody and C. O. R. de Barbarin, *J. Chem. Soc., Dalton Trans.*, 1987, 207; D. E. Fenton, S. J. Kitchen, C. M. Spencer, S. Tamburini and Vigato, *J. Chem. Soc., Dalton Trans.*, 1988, 685.
35 K. K. Nanda, S. K. Dutta, S. Baitalik, K. Venkatsubramanian and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1995, 1239; S. K. Dutta, R. Werner, U. Florke, S. Mohanta, K. K. Nanda, W. Haase and K. Nag, *Inorg. Chem.*, 1996, **35**, 2292.

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