Study of the Crystal Structure of Oxo-bridged Binuclear Fe^{III} Complex with Chiral Salen Ligand

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A oxo-bridged binuclear iron complex with chiral salen ligand $[Fe_2L_2]O$ (H_2L = *R*, *R'*-*N*, *N'*-bis(3,5-di-*tert*-butylsalicylaldene)-1,2-cyclohexanediamine) has been synthesized and the structure has been determined by X-ray diffraction analysis. The title complex crystallizes in triclinic system with space group *P*-1. Crystal data: $a = 1.42555(14)$ nm, $b = 1.54889(15)$ nm, $c = 1.83662(17)$ nm, $\alpha = 103.873(2)°$, $\beta = 100.506(2)°$, $\gamma = 101.840(2)°$, $V = 3.7371$ nm^3, $D_c = 1.082$ g/cm^3 and $Z = 2$. In the complex, each iron center is penta-coordination and in distorted square-pyramidal environment. Two Fe^{III} atoms are intramolecularly bridged by an oxygen atom with Fe···Fe nonbond distance of 0.3517(3) nm.

Keywords Oxo-bridged binuclear Fe^{III} complex, crystal structure, chiral salen ligand

In 1889, the first salen ligand and its Cu^{II} complex has been prepared by Combes.[1] Since then, salen derivatives and their metal complexes have been synthesized and characterized and gradually their values as catalysts have become recognized.[2] In the last decade, with the growth in interest in enantiomerically pure compounds for pharmaceutical and agrochemical industries, the development of metal complexes with chiral salen ligand as asymmetric catalysts has stimulated a very rapid growth in the chemistry of these species.[3-6] Meantime, μ-oxo-bridged binuclear iron complexes have attracted great interest in recent years.[7] From 1983 a renewed activity, driven by the endeavor to understand the chemistry of diiron in the non-heme proteins hemerythrin, ribonucleotide reductase, and the purple acid phosphatases, has been apparent in the literatures.[8] Moreover, the magnetic properties of the μ-oxo-bridged complexes such as $[\{Fe(salen)\}_2O]$ ($salenH_2$ = *N*, *N'*-bis(salicylidene)ethylenediamine) and $[\{Fe(saloph)\}_2O]$ ($salophH_2$ = bis(salicylidene)-*o*-phenylenediamine), have proved to be particularly interesting, and the magneto-structural correlations have been mentioned in many works.[9-14]

As a part of our devotion, we report herein the preparation and characterization of an optically active penta-coordination salen Fe^{III} complex (Fig. 1) and the structure has been determined by X-ray diffraction.

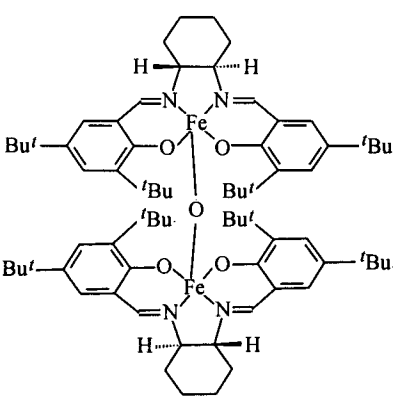

Fig. 1 Optically active penta-coordination sale Fe^{III} complex.

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Experimental

Materials and general methods

All the reagents for syntheses and analyses were of analytical grade. The chiral salen ligand *R*, *R'*-*N*, *N'*-bis(3,5-di-*tert*-butylsalicylaldene)-1,2-cyclohexane-diamine was synthesized according to the literature method.[15] The R configuration enantiomeric purity of the diamine resoluted by *L*-(+)-tartaric acid was determined by HPLC and circular dichroism (CD) (Fig. 2). FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) and electronic absorption spectra with a Shimadzu UV-260 spectrometer. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer 240C analyzer. Conductivitity of the complex was taken at room temperature using a DDS 11A conductometer.

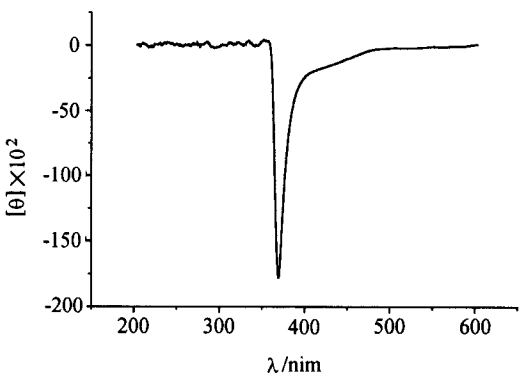

Fig. 2 Circular dichroism of the H_2L.

Synthesis of the title complex, $[Fe_2L_2]O$

It should be noted that the title complex was first synthesized by Wang-Hung Leung and co-workers[16] with stirring the ligand and $FeCl_3$ salt in the presence of excess NEt_3 in methanol solution. Here we report the title complex prepared by the method shown below and its X-ray single crystal which have never been reported until now.

To a suspension of H_2L (1.01 g, 1.84 mmol) in methanol (30 mL) was added equivalent of $FeCl_3 \cdot 4H_2O$ (0.37 g, 1.85 mmol) and the resultant mixture was stirred at room temperature for *ca*. 2 h. The brown precipitate was collected and dissolved in CH_2Cl_2. Purple compound of [FeL]Cl was obtaind. Yield: 0.81 g (70%). The title complex was prepared by stirring [FeL]Cl (1.27 g, 2 mmol) with NaClO (0.075 g, 1 mmol) in $NH_3 \cdot H_2O$ (20 mL) solution. The resultant mixture was chromatographed twice on a column packed with silicon gel (300—400 mesh) and eluted with chloroform and *n*-hexane. The first fraction that came off the column was [FeL]Cl and the second fraction was $[Fe_2L_2]O$ dimer. The CH_2Cl_2 solution of the power was left to stand at room temperature and single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. IR (KBr pellet) ν: 1616.8(vs), 1548.7(s), 1534.1(m), 1463.9(m), 1433.7(m), 866.3(s) cm^{-1}. UV-vis (ε/$dm^3 \cdot mol^{-1} \cdot cm^{-1}$) ($CH_2Cl_2$) λ_{max}: 383 (5500), 243 (29000) nm. Λ_M(CH_2Cl_2): 0.076 $cm^2 \cdot \Omega^{-1} \cdot mol^{-1}$. Anal. Calcd for $C_{72}H_{104}Fe_2N_4O_5$: C 71.0, H 8.6, N 4.6; Found: C 70.6, H 8.7, N 4.5.

Crystallographic study

Single-crystal X-ray diffraction measurement was carried out with a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo K_α radiation ($\lambda = 0.071073$ nm). Unit cell dimensions were obtained with least-squares refinements in the range of 1.40—25.03° and the structure was solved by direct method using the SHELXS-97 and SHELXL-97 package[17] and semi-empirical absorption corrections (SADABS) were applied. Fe atoms were located from *E*-maps and the other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was reformed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. Crystallog raphic data and experimental details for structural analyses are summarized in Table 1.

Table 1 Crystallographic data and structure refinement summary

Formula	$C_{72}H_{104}Fe_2N_4O_5$
M_T	1217.29
Crystal system	Triclinic
Space group	*P*-1
Temp. (K)	293 ± 2
a (nm)	1.42555(14)

Continued

b (nm)	1.54889(15)
c (nm)	1.83662(17)
α (deg)	103.873(2)
β (deg)	100.506(2)
γ (deg)	101.840(2)
V (nm^3)	3.7371(6)
D_c (g/cm^3)	1.082
Z	2
R	0.0636
R_w	0.1588
Reflections collected	15051
Independent reflections	12702
Goodness-of-fit	0.980
Max. Res. Peak (e/nm^3)	0.650×10^{-3}

Results and discussion

General characterization

The main difference of the IR spectra between the [FeL]Cl and $[Fe_2L_2]O$ are at 866.3 cm^{-1}, which is in the region of the antisymmetric Fe-O-Fe spectrum expected to occur.[18] It also shows absorption bands resulting from the skeletal vibration of aromatic ring in 1400—1600 cm^{-1} region. The conductivity value of the title complex indicates that it behaves as non-electrolyte in CH_2Cl_2 solution, which is consistent with the result of the X-ray analysis. The UV-vis spectra of the dimer, $[Fe_2L_2]O$ in CH_2Cl_2 solution have one strong absorption ligand-to-metal charge transfer (LMCT) in 383 nm and π-π^* transfer of the ligand at 243 nm.

Description of the crystal structure

The ORTEP view of the title complex including the atomic numbering scheme is given in Fig. 3. Relevant bond distances and angles have been listed in Table 2.

The structure of the oxo-bridged complex consists of neutral binuclear entity. The two Fe^{III} centers are bridged almost equivalently by one oxygen atom. The bridging oxygen are bound to each Fe^{III} at the distances of 0.1768(3) and 0.1750(3) nm, respectively, which is a little shorter than that in literature result (0.179 nm).[19] indicating stronger coordination of Fe—O bond. The Fe-O-Fe angle (176.4(2)°) is much larger than that in $[Fe_2(salen)_2]O$, (144.6°)[20] which is the stero-chemistry requirement due to the bulky size of *tert*-butyl.

Table 2 Selected bond distances ($\times 10^{-1}$ nm) and angles (°)

Fe(1)—O(1)	1.912(3)	Fe(1)—O(2)	1.925(3)
Fe(1)—N(1)	2.090(3)	Fe(1)—N(2)	2.098(3)
Fe(1)—O(5)	1.768(3)	Fe(2)—O(3)	1.918(3)
Fe(2)—O(4)	1.922(3)	Fe(2)—N(3)	2.090(3)
Fe(2)—O(5)	1.750(3)	Fe(2)—N(4)	2.099(3)
O(1)-Fe(1)-O(2)	93.60(12)	O(1)-Fe(1)-N(1)	86.48(12)
O(2)-Fe(1)-N(1)	139.03(14)	O(1)-Fe(1)-N(2)	151.59(14)
O(2)-Fe(1)-N(2)	85.00(12)	N(1)-Fe(1)-N(2)	76.53(13)
O(3)-Fe(2)-O(4)	94.59(13)	O(3)-Fe(2)-N(3)	86.48(12)
O(4)-Fe(2)-N(3)	137.33(14)	O(3)-Fe(2)-N(4)	152.86(14)
O(4)-Fe(2)-N(4)	84.57(13)	N(3)-Fe(2)-N(4)	76.30(13)
Fe(2)-O(5)-Fe(1)	176.4(2)		

Each Fe^{III} atom is bound by five donor atoms and the coordination geometry around Fe^{III} can be best described as a distorted square-pyramid with $\tau = 0.21$ (for Fe(1)) *vs*. 0.26 (for Fe(2)).[21] Two nitrogen donors and two oxygen atoms of the ligand comprise the basal plane, and the axial coordination site is occupied by the bridging oxygen atom. The Fe^{III} ions deviate from the mean equatorial plane of the square-pyramid towards the apical O(5) by *ca*. 0.046 nm for each Fe^{III} center. The ligand give rise with the central Fe^{III} ion to four six-membered chelate rings N(1)-C(1)-C(32)-C(31)-O(1)-Fe(1), N(2)-C(2)-C(42)-C(41)-O(2)-Fe(1), N(3)-C(3)-C(62)-C(61)-O(3)-Fe(2) and N(4)-C(4)-C(52)-C(51)-O(4)-Fe(2), forming N(1)-Fe(1)-

O(1) angle of 86.48(12)°, N(2)-Fe(1)-O(2) angle of 85.00(12)°, N(3)-Fe(2)-O(3) angle of 86.48(12)°, and N(4)-Fe(2)-O(4) angle of 84.57(13)°, which are quite similar and stabilize the crystal structure. The chiral carbon atoms of the cyclohexane in the complex that do not take part in the coordination reaction, still remain the *R* configuration as in the case of the free ligand. In addition, no weak interactions such as hydrogen bonds have been found to exist in the unit cell.

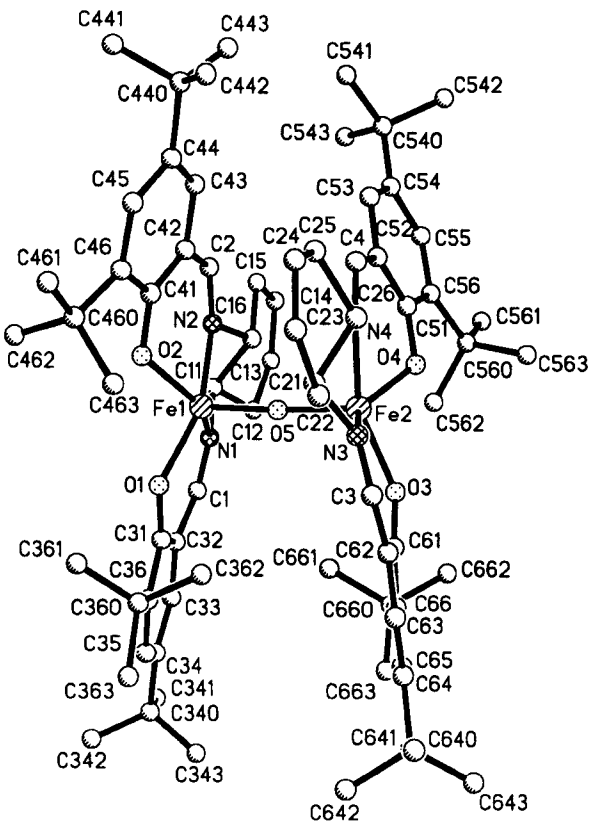

Fig. 3 Crystal structure of the title complex with 30% thermal ellipsoid probability.

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