Crystal structures of bis(cyclopentadienyldicarbonyliron)sodium tetrahydrofuran and (cyclopentadienyldicarbonyliron)sodium tetramethylethylenediamine complexes

Ninghai Hu, Guojun Nie, Zhongsheng Jin, and Wenqi Chen *

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun (China)

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Abstract

The extremely air-sensitive intermediate product $[C_5H_5Fe(CO)_2]_2Na \cdot 4THF$ (I) and final product $[C_5H_5Fe(CO)_2]Na \cdot TMEDA$ (II) have been obtained by the reduction of $[C_5H_5Fe(CO)_2]_2$ by Na/Hg. Their crystal structures have been determined at low temperature. The crystals belong to the monoclinic space group $P2_1/n$ with a 10.155(5), b 17.121(4), c 18.667(6) Å, and β 97.61(3)° for I, and to the orthorhombic space group $P2_12_12_1$ with a 6.001(4), b 10.644(6) and c 24.214(11) Å for II, respectively. Complex I has a linear chain structure with dimer anion $[C_5H_5Fe(CO)_2]_2^-$ and complex cation $(Na \cdot 4THF)^+$ connected alternately by Na–O(CO) bonds. Complex II has a spiral chain structure in which Na^+ with a TMEDA molecule and $(C_5H_5Fe)^-$ are bridged by carbonyl groups. A possible reaction mechanism based on the crystal structure is proposed.

Introduction

The interest in bimetallic complexes of lanthanides has been extended owing to their special behaviour in organic syntheses and catalytic reactions. In past years, the syntheses and structures of various binuclear complexes of lanthanide and transition metals have been described [1,2]. The reaction of lanthanide chlorides with the sodium salts of transition metal carbonyls is an important route to the binuclear complexes of lanthanide and transition metals. During the reduction of $[C_5H_5Fe(CO)_2]_2$, by Na/Hg to give the bimetallic complexes, we isolated the intermediates $[C_5H_5Fe(CO)_2]_2Na \cdot 4THF$ (I) and $[C_5H_5Fe(CO)_2]Na \cdot TMEDA$ ** (II). Further reaction of $LnCl_3 \cdot nTHF$ with I should give the binuclear complex of

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* Author to whom correspondence should be addressed.
** TMEDA = N,N,N',N'-tetramethylethylenediamine.

lanthanide and iron [3]. The structural studies of I and II should elucidate the reaction mechanism and enrich the chemistry of bimetallic complexes.

Here we report on the preparations of I and II, and describe their crystal structures.

Experimental

1. [C₅H₅Fe(CO)₂]₂Na · 4THF (I)

1. $[C_5H_5Fe(CO)_2]_2Na \cdot 4THF$ (I)

$[C_5H_5Fe(CO)_2]_2$ (0.9 g, 0.0025 mol) was added to a solution of Na/Hg in tetrahydrofuran(THF) under nitrogen. After 6–7 h stirring the reaction mixture was left to stand. The solution was centrifuged to removed the solid, and to the clear solution was added petroleum ether to give the dark-red crystals upon cooling.

2. $[C_5H_5Fe(CO)_2]Na \cdot TMEDA$ (II)

The procedure is similar to that for I, with 15 h stirring. The solution was centrifuged to remove the solid, to the resulting solution was added tetramethyleth-ylenediamine, and then petroleum ether to afford yellow needle-like crystals upon cooling.

3. Crystal structure

Both I and II, especially I, are extremely air-sensitive. Suitable crystals of I and II were selected under dry, cold nitrogen. The unit cell parameters were determined and the X-ray intensity data were collected on a Nicolet R3m/E four-circle diffractometer equipped with an LT-1 low temperature device, at about $-80°$C.

Table 1

Crystal data

Complex	I	II
Molecular formula	$C_{30}H_{42}O_8Fe_2Na$	$C_{13}H_{21}O_2N_2FeNa$
Molecular weight	665.3	316.2
Crystal size (mm³)	$0.3 \times 0.2 \times 0.3$	$0.2 \times 0.4 \times 0.1$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a (Å)	10.155(5)	6.001(4)
b (Å)	17.121(4)	10.644(6)
c (Å)	18.667(6)	24.214(11)
β (°)	97.61(3)	
V (Å³)	3216.9	1546.7
Z	4	4
D_c (g cm⁻³)	1.37	1.36
μ (cm⁻¹, MoK_α)	9.9	10.3
$2\theta_{max}$ (°)	40	42
Unique observed reflections $I > 3\sigma(I)$	1267	810
R	0.082	0.033
R_w	0.084	0.032
$\Delta\rho$ (e/Å³)	0.454	0.267
GOF	0.538	1.163

Table 2

Coordinates ($\times 10^4$) of non-hydrogen atoms

Atom	x	y	z	Atom	x	y	z
Complex I							
Fe(1)	3525(2)	7929(1)	1176(1)	O(51)	3567(23)	6237(12)	− 1514(13)
Fe(2)	5772(2)	8003(1)	731(1)	C(51)	3927(42)	5788(19)	− 2087(10)
Na	2205(7)	7361(3)	− 1526(3)	C(52)	4648(41)	5093(17)	− 1742(17)
O(1)	3510(12)	7718(6)	− 372(5)	C(53)	5280(36)	5445(24)	− 1045(18)
O(2)	5859(11)	7865(6)	2296(5)	C(54)	4119(40)	5906(20)	− 849(10)
O(3)	6656(17)	6400(11)	591(9)	O(61)	746(22)	6520(11)	− 994(9)
O(4)	3031(18)	6287(7)	1360(8)	C(61)	713(32)	6635(19)	− 244(10)
C(1)	4047(15)	7804(7)	229(9)	C(62)	− 282(41)	6070(24)	− 38(14)
C(2)	5298(14)	7893(8)	1669(8)	C(63)	− 1237(23)	6041(24)	− 716(22)
C(3)	6329(16)	7022(14)	653(8)	C(64)	− 300(30)	6010(18)	− 1266(12)
C(4)	3277(15)	6928(11)	1254(9)				
C(11)	2657(20)	9025(10)	953(10)	*Complex II*			
C(12)	3142(22)	9003(10)	1710(11)	Fe	− 983(2)	5241(1)	4283(1)
C(13)	2469(21)	8371(15)	1978(11)	Na	5951(5)	7324(2)	3963(1)
C(14)	1425(24)	8180(15)	1426(18)	O(1)	− 842(10)	6944(4)	5218(2)
C(15)	1669(20)	8483(12)	771(14)	O(2)	2308(8)	6768(4)	3721(2)
C(21)	5931(20)	9016(11)	134(11)	C(1)	− 983(14)	6256(6)	4839(3)
C(22)	6330(24)	9125(11)	900(16)	C(2)	939(13)	6156(5)	3957(2)
C(23)	7421(23)	8722(16)	1058(12)	C(11)	− 3741(15)	4036(7)	4400(3)
C(24)	7941(27)	8403(20)	502(19)	C(12)	− 3508(13)	4269(6)	3847(3)
C(25)	6787(21)	8463(12)	− 78(10)	C(13)	− 1401(14)	3832(6)	3695(3)
O(31)	3636(5)	8088(12)	− 2118(7)	C(14)	− 324(14)	3334(6)	4157(3)
C(31)	3406(30)	8337(18)	− 2843(8)	C(15)	− 1830(18)	3463(6)	4600(3)
C(32)	4352(28)	8995(22)	− 2945(15)	N(1)	6463(11)	7732(5)	2898(2)
C(33)	5297(40)	8812(28)	− 2272(17)	N(2)	7414(11)	9471(5)	3845(2)
C(34)	5009(17)	8082(27)	− 1867(27)	C(21)	7241(16)	9035(7)	2849(3)
O(41)	830(12)	8432(6)	− 1405(7)	C(22)	8479(16)	9539(8)	3297(3)
C(41)	− 520(23)	8488(15)	− 1672(21)	C(23)	8090(14)	6838(8)	2692(3)
C(42)	− 1026(22)	9245(13)	− 1604(16)	C(24)	4432(13)	7599(7)	2576(3)
C(43)	41(26)	9636(13)	− 1109(16)	C(25)	9137(14)	9613(6)	4259(3)
C(44)	1278(22)	9209(10)	− 1195(14)	C(26)	5776(15)	10437(7)	3917(3)

Graphite-monochromated MoK$_\alpha$ radiation and the scanning mode ω–2θ were used. The intensities were corrected for Lorentz and polarization factors. The crystal data are listed in Table 1.

The crystal structures for I and II were solved by heavy-atom method. There are two independent Fe atoms in I and only one in II as derived from the Patterson analyses. The coordinates of the Fe atoms were used to calculate Fourier maps. The preliminary structural models were established from all of the non-hydrogen atoms that had been located in successive Fourier syntheses. The structural parameters were refined by block-diagonal least-squares method and were weighted as follows

$$w = [\,\sigma^2(F) + |(g)F^2\,|\,]^{-1}$$

All calculations were by an Eclipse S/140 computer in SHELXTL programs. For I and II, the atomic coordinates and bond lengths and angles are listed in Tables 2, 3 and 4, respectively.

Table 3

Main bond lengths (Å) and angles (°) for complex I [a]

Fe(1)–Fe(2)	2.534(3)	Fe(1)–C(1)	1.92(2)
Fe(1)–C(2)	1.91(1)	Fe(1)–C(4)	1.74(2)
Fe(2)–C(1)	1.91(2)	Fe(2)–C(2)	1.89(2)
Fe(2)–C(3)	1.78(2)	C(1)–O(1)	1.19(2)
C(2)–O(2)	1.23(2)	C(3)–O(3)	1.13(3)
C(4)–O(4)	1.15(2)	Fe(1)–C(11)	2.09(2)
Fe(1)–C(12)	2.15(2)	Fe(1)–C(13)	2.09(2)
Fe(1)–C(14)	2.28(3)	Fe(1)–C(15)	2.16(2)
Fe(2)–C(21)	2.08(2)	Fe(2)–C(22)	2.02(2)
Fe(2)–C(23)	2.10(2)	Fe(2)–C(24)	2.40(3)
Fe(2)–C(25)	2.09(2)	C(11)–C(12)	1.43(3)
C(12)–C(13)	1.41(3)	C(13)–C(14)	1.42(3)
C(14)–C(15)	1.38(4)	C(15)–C(11)	1.38(3)
C(21)–C(22)	1.45(4)	C(22)–C(23)	1.31(3)
C(23)–C(24)	1.34(4)	C(24)–C(25)	1.49(4)
C(25)–C(21)	1.38(3)	Na–O(1)	2.45(1)
Na–O(2′)	2.46(1)	Na–O(31)	2.31(2)
Na–O(41)	2.34(1)	Na–O(51)	2.37(2)
Na–O(61)	2.38(2)		
Fe(2)–Fe(1)–C(4)	102.8(5)	C(1)–Fe(1)–C(2)	94.7(7)
C(1)–Fe(1)–C(4)	91.5(7)	C(2)–Fe(1)–C(4)	83.9(6)
Fe(1)–Fe(2)–C(3)	106.8(6)	C(1)–Fe(2)–C(2)	96.2(7)
C(1)–Fe(2)–C(3)	94.1(7)	C(2)–Fe(2)–C(3)	96.0(7)
Fe(1)–C(1)–Fe(2)	82.9(6)	Fe(1)–C(1)–O(1)	137.1(13)
Fe(2)–C(1)–O(1)	139.6(14)	Fe(1)–C(2)–Fe(2)	83.7(6)
Fe(1)–C(2)–O(2)	138.2(12)	Fe(2)–C(2)–O(2)	138.0(12)
Fe(2)–C(3)–O(3)	178.3(12)	Fe(1)–C(4)–O(4)	172.8(17)
C(1)–O(1)–Na	170.4(11)	C(2)–O(2)–Na′	170.6(10)
O(1)–Na–O(2′)	174.6(4)		

[a] Na′ and O(2′) are generated by transformations $0.5 + x$, $1.5 - y$, $0.5 + z$ and $-0.5 + x$, $1.5 - y$, $-0.5 + z$, respectively.

Results and discussion

The structure of I can be regarded as an infinite chain composed of the complex cation (Na · 4THF)$^+$ and the complex anion $[C_5H_5Fe(CO)_2]_2^-$, which are alternatively connected by Fe–O(carbonyl) bonds. Fig. 1 shows single unit of the chain structure.

It is known that for the *cis-* and *trans-*isomer of the $[C_5H_5Fe(CO)_2]_2$ dimer the bond lengths and angles are almost equivalent, but they differ in the angle between the bridging planes Fe(1)–C(1)–Fe(2) and Fe(1)–C(2)–Fe(2), which is 180° for the *trans-*isomer because of the symmetric centre compared with 164° for the *cis-*isomer [4]. As is seen in Fig. 1, $[C_5H_5Fe(CO)_2]_2^-$ anion remains a dimer. Each Fe atom is coordinated by an η^5-cyclopentadienyl, two bridging and one terminal carbonyl groups, and forms an Fe–Fe bond with another Fe atom. Two terminal carbonyl groups are located on one side of the plane of the Fe_2C_2 ring while the cyclopentadienyl rings are on the other side of the plane, thus $[C_5H_5Fe(CO)_2]_2^-$ exhibits *cis-*conformation with an angle of 163.7° between the bridging planes of Fe–C–Fe. The bond lengths of Fe–Fe, Fe–C(bridging) and Fe–C(terminal) in I are almost

Table 4

Bond lengths (Å) and angles (°) for complex II [a]

Fe–C(1)	1.727(6)	Fe–C(2)	1.704(7)
Fe–C(11)	2.113(8)	Fe–C(12)	2.116(7)
Fe–C(13)	2.084(7)	Fe–C(14)	2.091(6)
Fe–C(15)	2.104(7)	Na–O(1)	2.388(5)
Na–O(2)	2.339(6)	Na–N(1)	2.632(6)
Na–N(2)	2.464(6)	O(1)–C(1)	1.176(7)
O(2)–C(2)	1.194(8)	C(11)–C(12)	1.369(10)
C(12)–C(13)	1.397(11)	C(13)–C(14)	1.397(11)
C(14)–C(15)	1.410(12)	C(15)–C(11)	1.385(13)
N(1)–C(21)	1.468(9)	N(1)–C(23)	1.452(10)
N(1)–C(24)	1.455(10)	N(2)–C(22)	1.475(9)
N(2)–C(25)	1.447(10)	N(2)–C(26)	1.434(10)
C(21)–C(22)	1.421(11)		
C(1)–Fe–C(2)	90.2(3)	Fe–C(1)–O(1)	175.9(7)
Fe–C(2)–O(2)	178.2(5)	C(1)–O(1)–Na'	152.0(5)
C(2)–O(2)–Na	131.5(4)	O(2)–Na–O(1')	82.5(2)
O(2)–Na–N(1)	84.6(2)	O(2)–Na–N(2)	122.6(2)
O(1')–Na–N(1)	144.3(2)	O(1')–Na–N(2)	87.4(2)
N(1)–Na–N(2)	72.1(2)	C(15)–C(11)–C(12)	109.6(7)
C(11)–C(12)–C(13)	106.9(7)	C(12)–C(13)–C(14)	109.4(7)
C(13)–C(14)–C(15)	106.0(7)	C(14)–C(15)–C(11)	108.0(6)
Na–N(1)–C(21)	105.9(4)	Na–N(1)–C(23)	107.9(4)
Na–N(1)–C(24)	114.3(4)	C(21)–N(1)–C(23)	112.2(6)
C(21)–N(1)–C(24)	108.3(6)	C(23)–N(1)–C(24)	108.4(5)
Na–N(2)–C(22)	107.7(4)	Na–N(2)–C(25)	105.7(4)
Na–N(2)–C(26)	114.0(5)	C(22)–N(2)–C(25)	108.0(6)
C(22)–N(2)–C(26)	111.8(6)	C(25)–N(2)–C(26)	109.3(5)
N(1)–C(21)–C(22)	117.4(6)	C(21)–C(22)–N(2)	116.2(8)

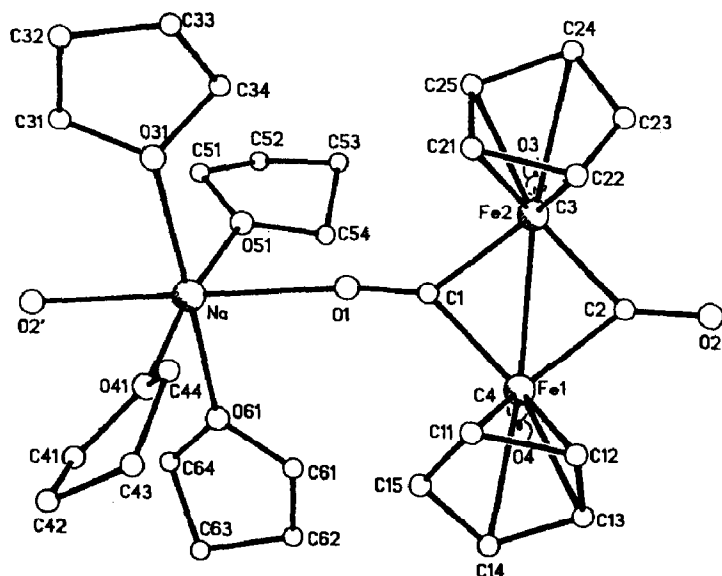[a] Na' and O(1') are generated by transformations $-0.5 + x$, $1.5 - y$, $1 - z$ and $0.5 + x$, $1.5 - y$, $1 - z$, respectively.

Fig. 1. Structure of $[C_5H_5Fe(CO)_2]_2Na \cdot 4THF$ (I).

Table 5

Comparison of bond lengths (Å) [a]

Bond	trans-[$C_5H_5Fe(CO)_2$]$_2$	cis-[$C_5H_5Fe(CO)_2$]$_2$	I	II
Fe–Fe	2.534	2.531	2.534	2.983 (Fe–Na)
Fe–C(b)	1.914	1.917	1.91	
Fe–C(t)	1.748	1.745	1.76	1.716 (Fe–C)
Fe–C(ring)	2.106	2.114	2.15	2.102
		2.104	2.14	
C–O(b)	1.188	1.181	1.21	
C–O(t)	1.157	1.153	1.14	1.185 (C–O)
Na–O(CO)			2.46	2.364

[a] Average values are given.

identical with those observed in the *cis*- and *trans*-isomers of [$C_5H_5Fe(CO)_2$]$_2$ (Table 5), which suggests that the three complexes are energetically equivalent, and that I can be separated as an intermediate product.

In I the Na$^+$ ion is six coordinate and occupies the centre of an octahedron. The μ_3-carbonyl is associated with three metal atoms, viz., the carbon atom forms two single bonds with the two Fe atoms, and the oxygen atom provides a pair of electrons to coordinate to Na$^+$. The average bond angles, Na–O–C of 170.5°, and O–Na–O of 174.6° are approximately linear.

In complex II each Fe atom complexed with a η^5-cyclopentadienyl group is indirectly connected to two Na$^+$ ions attached to two chelating TMEDA molecules by two asymmetric bridging carbonyl groups; similary each Na$^+$ ion is linked to two Fe atoms, and so a spiral chain structure is formed (Fig. 2). The repeat unit of spiral
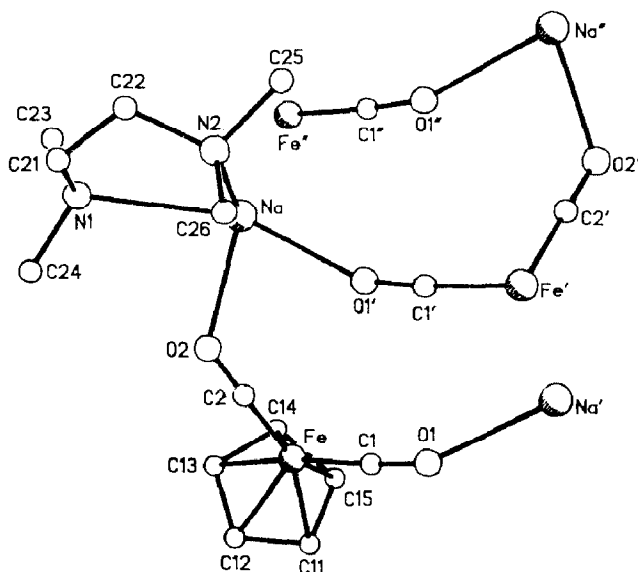
Fig. 2. Structure of [$C_5H_5Fe(CO)_2$]Na·TMEDA (II).

chain is $\{[C_5H_5Fe(CO)_2]Na \cdot TMEDA\}_2$ and the "screw pitch" is consistent with the "a" translation.

The oxidation state of the Fe atom is regarded as zero, the same as in its carbonyl complexes. A cyclopentadienyl group provides six π-electrons to interact with the Fe atom with the average Fe–C(ring) of 2.102 Å very similar to that in the $[C_5H_5Fe(CO)_2]_2$ molecule and slightly longer than that in ferrocene (2.033 Å) [5]. In addition, the carbon atoms of both carbonyl groups coordinate individually to Fe with a pair of their own electrons to satisfy the 18-electron rule. The bond length of Fe–C(carbonyl) is slightly shorter than those of Fe–C(terminal) in the other three complexes but the bond length of C–O is longer than those of C–O(t), which incidates a strong interaction between the metal atoms and the carbonyl resulting in activation of the carbonyl (Table 5).

The Na^+ and four coordinating atoms form a tetragonal pyramid with Na^+ at the apex. Because Na^+ is loosely bonded to Fe'' (2.983 Å) and $C(1)''$ (3.030 Å) in the direction of the apex of the pyramid, it undergoes preferential attack by a nucleophile at this site.

The results of the X-ray diffraction studies suggest that in the reaction starting from $[C_5H_5Fe(CO)_2]_2$ to give II the sodium atom first interacts with the oxygen of the bridging carbonyl to form the comparatively stable intermediate I, further reaction opens the Fe–C(bridging) single bonds in $[C_5H_5Fe(CO)_2]_2^-$ and at the same time, sodium is bonded to oxygen atoms of the terminal carbonyl groups to give the spiral chain structure II. In the above reaction, with the change in the oxidation state of Fe from $+1$ to zero via the intermediate state, the iron atom takes on the stable 18-electron configuration again. This accounts for the fact that II was observed to be more stable than I.

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