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Crystal Structure of Mixed-valence Compound 1′,1‴-Dipropylbiferrocenium Triiodide with Averaged-valence Type Irons at 298 K and with Trapped-valence Type Irons at 110 K and Thermal Electron Transfer Process of Mono-oxidized Binuclear Ferrocene Derivatives

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The crystal structure of 1′,1‴-dipropylbiferrocenium $\mathrm{(PrFcFcPr)^+I_3^-}$, which shows averaged-valence irons at 298 K and trapped-valence irons at 110 K, was determined by X-ray diffraction. The crystal at 298 K is triclinic, space group $P\bar{1}$, $a=8.5148(8)$, $b=8.5482(5)$, and $c=10.9032(13)$ Å, $\alpha=89.546(9)$, $\beta=115.582(9)$, and $\gamma=108.488(7)°$, $U=671.10(9)$ Å^3, and $Z=1$. The crystal at 110 K is triclinic, space group $P1$, $a=8.431(2)$, $b=8.478(2)$, and $c=10.816(3)$ Å, $\alpha=88.58(3)$, $\beta=117.39(2)$, and $\gamma=108.65(2)°$, $U=643.4(3)$ Å^3, and $Z=1$. Structures were refined to $R=0.042$ at 298 K and $R=0.050$ at 110 K. At 298 K cation $\mathrm{(PrFcFcPr)^+}$ sits on the symmetry center and the two Fc units are crystallographically equivalent, whereas at 110 K the symmetry center is lost and ferrocene-like and ferrocenium-like Fc units are distinguished. A three-dimensional hydrogen-bond network is clearly found between the cation and iodine atoms at 110 K, in contrast to the result at 298 K. Infrared spectra of 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium$\mathrm{^+I_3^-}$a nd μ-(as-indacenyl)-bis(cyclopentadienyliron)$\mathrm{^+I_3^-0.5I_2}$ salts measured at 294 and 78 K indicate that a remarkable change in peak intensity is observed at 680 and 1525 cm^{-1} in the dialkyl salts, whereas no change is found in the remainder.

A number of mono-oxidized salts of binuclear ferrocene derivatives have been investigated to clarify the electronic interaction between two metal sites and the electron transfer process,[1] especially in connection with Mössbauer spectroscopic behavior, electronic configuration, and magnetic and optical properties of these compounds. The compounds are classified roughly into two types: one is the mixed-valence or trapped-valence type which contains ferrocene-like bivalent and ferrocenium-like tervalent iron atoms, including biferrocenium$^+$,[2,3] diferrocenylacetylenium$^+$,[4] and diferrocenylselenium$^+$ [5] cations; the other is the averaged-valence type which contains equivalent iron atoms, including 1′,1‴-diiodobiferrocenium$^+$,[6] [2.2]ferrocenophane-1,13-diyne$^+$,[4] and biferrocenylenium$^+$ [7,8] cations.

Recently, it was reported that 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium$\mathrm{(PrFcFcPr)^+I_3^-}$ salts and μ-[1-3a(8b)-η : 6-8a(5a)-η-as-indacenyl]-bis(η-cyclopentadienyliron)$\mathrm{^+I_3^-0.5I_2}$ salt give rise to a transition from the averaged-valence state of iron atoms to the trapped-valence state as temperature is lowered.[9—11] In addition, in the latter salt the line-broadening of Mössbauer spectrum was observed at higher temperatures.

We determined the crystallographic change in $\mathrm{(PrFcFcPr)^+I_3^-}$ at 298 and 110 K, in order to clarify whether or not the transition in cation $\mathrm{(PrFcFcPr)^+}$ from the averaged-valence to the trapped-valence state is accompanied with structural changes and how anion $\mathrm{I_3^-}$ affects this transition. It has been known that unsubstituted cation biferrocenium$^+$ shows a temperature-independent trapped-valence state, whereas cation 1‴,1′-diiodobiferrocenium$^+$ shows a temperature-independent averaged-valence state. The present paper also provides information concerning the effect of the propyl group on the electronic state of the cation.

Although Mössbauer spectroscopy can distinguish whether or not the rate of the thermal electron transfer between two iron atoms in these salts is higher than *ca.* 10^7 s^{-1}, infrared spectroscopy involves a different time scale of *ca.* 10^{13} s^{-1}. By comparing infrared spectra of 1′,1‴-diethyl and 1′,1‴-dipropylbiferrocenium$\mathrm{^+I_3^-}$ salts and μ-(as-indacenyl)-bis(cyclopentadienyliron)$\mathrm{^+I_3^-0.5I_2}$ salt at 294 and 78 K with Mössbauer spectra, the difference in electronic state between these salts is discussed.

Experimental

X-Ray Measurements. Crystals in dark-red thin plate were sealed into Lindemann-glass capillaries filled with Ar gas, since they will break down when exposed to air. Preliminary oscillation and Weissenberg photographs were taken at room temperature by using Cu *Kα* radiation. The crystal was determined to be triclinic. The space group was later confirmed to be $P\bar{1}$ at 298 K and $P1$ at 110 K by structure refinements. The final unit cell dimensions are refined by the least-squares method based on θ values of 27 reflections at 298 K and of 18 reflections at 110 K.

The cooling equipment was constructed of stainless steel according to the description by Bolhuis.[12] Crystal specimens were cooled by a stream of cold N_2 gas which was surrounded by warmer N_2 gas. Temperature was maintained at 110±1 K electrically by monitoring with a chromel-almel thermocouple throughout the experiment.

Intensities were collected on an automated four-circle diffractometer with Ag *Kα* radiation monochromated by graphite. The absorption coefficient of elements for Ag *Kα* radiation is about half as large as that for Mo *Kα* radiation. Three standard reflections were observed every fifty reflections. Correction was made for Lorentz and polarization effects and for absorption. Crystal data and experimental conditions are summarized in Table 1.

Infrared Measurements. Infrared spectra were recorded

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TABLE 1. CRYSTAL DATA

$(Fe_2C_{26}H_{30})^+I_3^-$, M.W. 834.92		
Temperature/K	298	110
	Triclinic	Triclinic
Space group	$P\bar{1}$	P1
a/Å	8.5148(8)	8.431(2)
b/Å	8.5482(5)	8.478(2)
c/Å	10.9032(13)	10.816(3)
α/°	89.546(9)	88.58(3)
β/°	115.582(9)	117.39(2)
γ/°	108.488(7)	108.65(2)
U/Å^3	671.10(9)	643.4(3)
Z	1	1
D_x/g cm^{-3}	2.066	2.155
μ(Ag $K\alpha$)/mm^{-1}	2.23	2.33
Crystal size/mm	0.016×0.36×0.37	0.03×0.29×0.30
Scan method	ω-2θ	ω
$\sin\theta/\lambda_{max}$	0.682	0.682
Independent reflections ($\|F\| > 3\sigma$)	1928	2061
Maximum repeating number	3	1
$R=\sum\|\|F_o\|-\|F_c\|\|/\sum\|F_o\|$	0.042	0.050
$R_2=\{\sum(\|F_o\|-\|F_c\|)^2/\sum\|F_o\|^2\}^{1/2}$	0.043	0.075

on a Fourier-transform spectrometer (NICOLET 7199). All samples were prepared as KBr pellets 13 mm in diameter. For low temperature measurements, the sample mounted in a holder was cooled by a copper plate linked to liquid nitrogen in a Dewar with KRS-5 windows.

Structure Determination

High-temperature Phase (298 K). The structure was solved by the conventional heavy-atom method. The positions of Fe and I atoms were deduced from sharpened Patterson maps. Successive three-dimensional Fourier syntheses phased by these atoms yielded the positions of all C atoms. Difference Fourier maps clarified not only the positions of H atoms but also the existence of rotational disorder of propylcyclopentadienyl ring. Several cycles of full-matrix least-squares refinements were carried out by using the RADIEL program.[13] The population of disordered propylcyclopentadienyl was also refined so as to converge to the ratio 75 : 25. Anisotropic thermal parameters were used for non-hydrogen atoms and isotropic thermal parameters for hydrogen and carbon atoms of disordered propylcyclopentadienyl with low population. Atomic scattering factors for non-hydrogen atoms were taken from International Tables for X-Ray Crystallography,[14] and those for H atoms from Stewart *et al.*[15] Unit weights were adopted for all reflections. Refinements led to a convergence of R=0.042. Final atomic parameters are given in Table 2.†††

Low-temperature Phase (110 K). The starting coordinates of the low-temperature phase could readily be deduced from the atomic coordinates of the high-temperature phase. Several cycles of full-matrix least-squares refinements reduced the R value to 0.064 for the structure with space group $P\bar{1}$ without disorder. At this stage, difference Fourier syntheses showed not only rotational disorder of propylcyclopentadienyl but also positional disorder of triiodide. Refinements with these disorders considered gave R=0.055. The space group was assumed to be P1 with no symmetry center. The structure was assumed to consist of a ferrocene-like divalent unit and ferrocenium-like tervalent unit for cation (PrFcFcPr)$^+$. Anisotropic thermal parameters were used for the I, Fe, and C atoms of fulvalene moiety and isotropic thermal parameters for the C atoms of disordered propylcyclopentadienyls and H atoms. The populations of two types of disorders were also refined and R was converged to 0.050. The final difference Fourier maps showed peaks of about 1.0 eÅ^{-3} near anion I_3^-. The final atomic parameters are tabulated in Table 3.†††

Results and Discussion

Description of Crystal Structure. High-temperature Phase: *Packing*: Projections of the structure in the high-temperature phase along the a and c axes are shown in Figs. 1 and 2. (PrFcFcPr)$^+$ cations are stacked along the c axis in a plane-to-plane manner to form a column. The structure is dominated by segregated columns of cation (PrFcFcPr)$^+$ and anion I_3^-. The column of anion I_3^- is surrounded by four columns of the cations. The cation and anion are interacted by van der Waals' force between hydrogen atoms of the cation and iodine atoms as shown in Table 4. Figures 3(a) and (b) show packing views in the high- and low-temperature phases, respectively. Five-membered rings of propylcyclopentadienyls between neighboring (PrFcFcPr)$^+$ cations overlap as shown in Fig. 4(b). Their interplanar distance is 3.47(2) Å and an intermolecular interaction is expected

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††† Lists of structure factors and anisotropic thermal parameters in the high- and low-temperature phases and atomic parameters of hydrogen atoms in the low-temperature phase are kept in the Chemical Society of Japan as Document No. 8238.

Table 2. Positional parameters with e.s.d.'s in parentheses for the high-temperature phase (298 K)

a) I, Fe atoms ($\times 10^5$), and C atoms ($\times 10^4$)

Atom	x	y	z	$10^3U_{eq}/Å^2$	Population
I(1)	0	50000	0	55(0)	1.0
I(2)	10015(10)	43861(9)	28387(8)	68(0)	1.0
Fe	41961(17)	10776(15)	17719(13)	40(1)	1.0
C(1)	2614(11)	33(10)	−250(8)	38(4)	1.0
C(2)	2247(13)	1469(11)	9(10)	48(5)	1.0
C(3)	3899(14)	2845(12)	519(10)	49(5)	1.0
C(4)	5302(12)	2271(10)	547(9)	43(4)	1.0
C(5)	4519(11)	547(10)	51(8)	37(4)	1.0
C(6)	3910(35)	−556(19)	3126(17)	56(10)	0.75(2)
C(7)	3025(23)	662(24)	3085(16)	52(8)	0.75
C(8)	4578(35)	2129(31)	3596(24)	56(11)	0.75
C(9)	6327(26)	1907(26)	3798(15)	62(8)	0.75
C(10)	5819(25)	182(25)	3511(15)	50(8)	0.75
C(11)	7189(24)	−664(20)	3616(17)	65(9)	0.75
C(12)	6383(27)	−2491(23)	3164(18)	74(10)	0.75
C(13)	7875(36)	−3199(32)	3294(28)	68(13)	0.75

b) H and C atoms of propylcyclopentadienyl with the low population($\times 10^3$)

Atom	x	y	z	$10^3U/Å^2$	Population
C(6*)	301(7)	−76(7)	273(5)	38(11)	0.25
C(7*)	364(8)	108(7)	340(5)	33(11)	0.25
C(8*)	515(8)	240(8)	371(7)	35(15)	0.25
C(9*)	592(6)	118(7)	368(5)	36(10)	0.25
C(10*)	491(6)	−58(5)	314(4)	24(7)	0.25
C(11*)	560(5)	−193(4)	316(3)	35(9)	0.25
C(12*)	775(5)	−129(5)	362(4)	45(10)	0.25
C(13*a)	873(7)	−250(6)	329(6)	32(10)	0.19
C(13*b)	935(14)	−222(12)	411(11)	14(18)	0.06
H(C1)	170(11)	−103(9)	−62(8)	33(21)	1.0
H(C2)	109(12)	158(10)	−1(8)	48(24)	1.0
H(C3)	408(13)	393(12)	74(10)	61(29)	1.0
H(C4)	648(11)	294(9)	89(8)	32(21)	1.0
H(C6)	287(27)	−151(21)	279(18)	97(68)	0.75
H(C7)	203(10)	56(8)	278(7)	14(16)	0.75
H(C8)	476(16)	329(14)	365(11)	41(32)	0.75
H(C9)	742(18)	274(16)	407(13)	56(38)	0.75
H(C11a)	786(16)	−27(14)	297(12)	47(32)	0.75
H(C11b)	809(18)	−61(15)	459(14)	61(39)	0.75
H(C12a)	519(16)	−255(14)	224(12)	41(31)	0.75
H(C12b)	571(18)	−293(16)	364(13)	54(40)	0.75
H(C13a)	833(18)	−314(17)	385(12)	14(43)	0.75
H(C13b)	741(19)	−439(18)	314(14)	69(45)	0.75
H(C13c)	815(19)	−309(17)	270(13)	37(35)	0.75

to exist between the neighboring cations.

Structure of Cation $(PrFcFcPr)^+$: Each iron atom in a cation $(PrFcFcPr)^+$ is sandwiched by five-membered rings in *trans*-configuration. The cation sits on a symmetry center and the two Fc units are crystallographically equivalent. Therefore, electronic states of the two iron atoms are expected to be in an averaged-valence (+2.5) state. The interplanar distance between the two five-membered rings in a Fc unit is 3.33(2) Å and their dihedral angle is 6.6°. This ring-ring distance in the ferrocene-like unit was found to be 3.32 Å in the unoxidized compound biferrocene[16] and 3.277(19) Å in the trapped-valence salt diferrocenylselenium$^+$ iodine triiodide$^-$ hemi(dichloromethane),[5] whereas that for ferrocenium-like unit 3.40 Å in ferrocenium$^+$ tetrachlorobismuthate$^-$ [17] and 3.397(22) Å in cation diferrocenylselenium$^+$. Distances of the iron atom from the least-squares planes of two five-membered rings are found to be 1.656(5) Å for the fulvalene moiety and 1.678(13) Å for the propylcyclopentadienyl ring. Bond distances and bond angles are given in Table 5. Mean bond distances between the iron atom and five carbon atoms are 2.047(9) and 2.072(16) Å for the inner and outer rings, respectively. The mean distance between them is 2.059 Å, which lies midway between 2.045 Å for molecule ferrocene[18] and 2.075 Å for cation ferrocenium$^+$.[17]

The propylcyclopentadienyl ring is found to be

TABLE 3. POSITIONAL PARAMETERS WITH e.s.d.'s IN PARENTHESES FOR THE LOW-TEMPERATURE PHASE (110 K)

a) I, Fe, and C atoms of fulvalene moiety ($\times 10^4$)

Atom	x	y	z	$10^3U_{eq}/\text{Å}^2$	Population
I(1)	0(0)	5000(0)	0(0)	13(1)	0.90(1)
I(2)	1085(9)	4347(8)	2919(7)	24(2)	0.90
I(3)	−898(8)	5520(7)	−2876(7)	17(1)	0.90
Fe(1)	4279(14)	1076(13)	1803(10)	22(3)	1.0
Fe(2)	5902(12)	−1156(10)	−1716(10)	13(3)	1.0
C(1)	2585(55)	−43(59)	−390(50)	30(18)	1.0
C(2)	2204(55)	1362(58)	−118(46)	43(19)	1.0
C(3)	3773(45)	2778(32)	280(34)	10(10)	1.0
C(4)	5389(40)	2290(40)	549(28)	10(12)	1.0
C(5)	4582(71)	427(63)	110(49)	41(22)	1.0
C(14)	7585(47)	−51(39)	288(40)	16(11)	1.0
C(15)	7987(40)	−1414(33)	76(30)	14(10)	1.0
C(16)	6213(45)	−2952(49)	−525(36)	24(13)	1.0
C(17)	4781(49)	−2307(45)	−420(38)	32(15)	1.0
C(18)	5545(41)	−613(39)	22(34)	5(9)	1.0
I(1*)	1176(36)	4683(76)	2914(41)	144(31)	0.10
I(2*)	451(43)	5282(83)	254(36)	141(30)	0.10
I(3*)	−479(119)	6289(113)	−2849(49)	194(53)	0.10

b) C atoms of disordered propylcyclopentadienyls ($\times 10^3$)

Atom	x	y	z	$10^3U/\text{Å}^2$	Population
C(6)	387(6)	−68(6)	318(5)	13(9)	0.82(4)
C(7)	313(6)	48(6)	313(5)	26(10)	0.82
C(8)	483(11)	216(9)	373(8)	44(18)	0.82
C(9)	642(6)	195(6)	390(5)	9(9)	0.82
C(10)	572(9)	17(8)	347(6)	35(14)	0.82
C(11)	720(4)	−74(4)	369(4)	4(7)	0.82
C(12)	639(4)	−271(3)	326(3)	5(5)	0.82
C(13)	779(8)	−343(7)	338(6)	39(14)	0.82
C(19)	625(8)	61(7)	−299(5)	32(12)	0.89(4)
C(20)	691(4)	−90(5)	−315(3)	5(6)	0.89
C(21)	537(6)	−229(5)	−357(4)	6(7)	0.89
C(22)	372(7)	−199(6)	−374(5)	20(11)	0.89
C(23)	420(5)	−20(5)	−358(4)	3(7)	0.89
C(24)	278(6)	53(6)	−357(5)	31(10)	0.89
C(25)	373(5)	234(5)	−309(4)	28(9)	0.89
C(26)	227(5)	330(5)	−320(4)	10(7)	0.89
C(6*)	353(27)	−56(23)	333(17)	13	0.18
C(7*)	370(23)	104(21)	350(16)	13	0.18
C(8*)	521(24)	258(20)	381(18)	13	0.18
C(9*)	620(20)	126(22)	368(15)	13	0.18
C(10*)	492(24)	−26(17)	337(14)	13	0.18
C(11*)	511(17)	−197(14)	310(11)	13	0.18
C(12*)	745(21)	−146(20)	366(15)	13	0.18
C(13*)	840(19)	−277(17)	352(16)	13	0.18
C(19*)	678(39)	50(36)	−293(29)	13	0.11
C(20*)	630(39)	−155(35)	−323(26)	13	0.11
C(21*)	494(34)	−254(30)	−330(26)	13	0.11
C(22*)	387(32)	−139(33)	−399(25)	13	0.11
C(23*)	425(47)	17(37)	−366(32)	13	0.11
C(24*)	414(32)	164(25)	−321(20)	13	0.11
C(25*)	269(39)	117(37)	−354(27)	13	0.11
C(26*)	135(29)	233(26)	−342(23)	13	0.11

rotationally disordered, with two sites in population ratio 75 : 25, as shown in Fig. 4(a). The two sites are related to each other by a pseudo-mirror plane normal to the fulvalene moiety and passing through the C(5)–C(5′) bond. The outer ring with the high population and the five-membered ring of the fulvalene moiety are mutually displaced by about 0.5 Å in their gravity centers, are mutually rotated away from the eclipsed

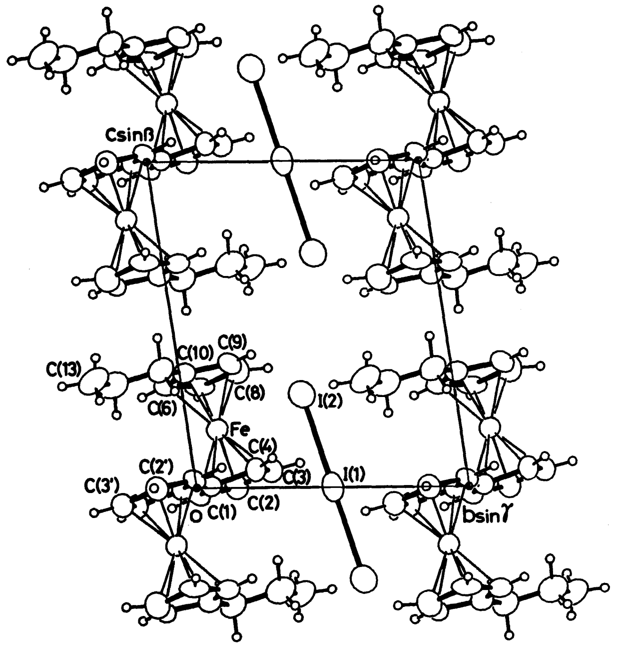

Fig. 1. The projection of the structure for the high-temperature phase (298 K) along the a axis.

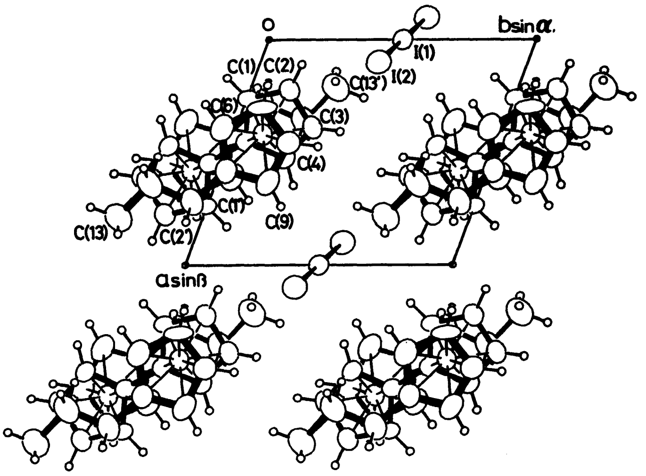

Fig. 2. The projection of the structure for the high-temperature phase (298 K) along the c axis.

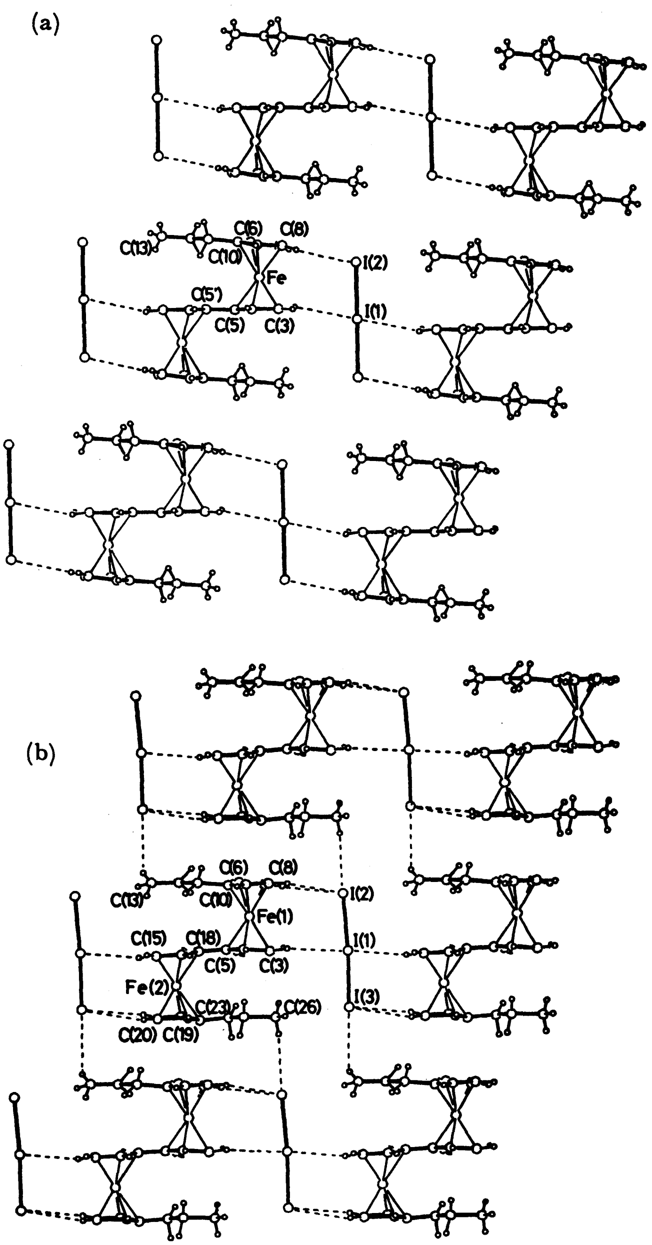

Fig. 3. Packing views in the (110) plane (a) for the high-temperature phase (298 K) and (b) for the low-temperature phase (110 K). Broken lines show short contacts between hydrogen and iodine atoms.

conformation by 10° in the mean value, and remain in a nearly eclipsed conformation. On the other hand, for the site with the low population the Fc unit is rotated in the opposite direction by about 15° and is about midway between eclipsed (0°) and staggered (36°) positions. Molecule ferrocene is known to take a nearly eclipsed conformation with a rotational angle of 9° in the disordered high-temperature phase and in the ordered low-temperature phase.[18,19] Rotational angles were observed to be 17, 3.6, 5.2, and 4.1° for biferrocene, 1',1'''-diethylbiferrocene, 1',1'''-dichlorobiferrocene, and 1',1'''-diacetylbiferrocene,[16,20–22] respectively.

Data of some least-squares planes and deviations of atoms from their planes are given in Table 6. The dihedral angle between the planes of five-membered ring and propyl group within propylcyclopentadienyl is 3.5° and they sit essentially coplanar. The propyl group is also parallel to the fulvalene plane and sits at the position above the ring of the other sandwich of the fulvalene moiety deviating from the ideal position overlapped between their C–C bonds. This is in contrast to the unoxidized compound 1',1'''-diethylbiferrocene, in which the ethyl group is not parallel to the fulvalene moiety and stands away from it.[20] Hydrogen atoms H(11a) and H(12a) in the propyl group are situated at 2.77(12) and 2.86(12) Å from the least-squares plane of the fulvalene moiety. There seems to exist a strong interaction within the cation between the propyl group

TABLE 4. INTERMOLECULAR DISTANCES (l/Å) SHORTER THAN 3.4 Å BETWEEN HYDROGEN ATOMS OF (PrFcFcPr)$^+$ CATION AND IODINE ATOMS

Symmetry code							
None	x,	y,	z	(iv)	$-1+x$,	$1+y$,	z
(i)	$-x$,	$-y$,	$-z$	(v)	$-1+x$,	$1+y$,	$-1+z$
(ii)	$-1+x$,	y,	z	(vi)	x,	$1+y$,	z
(iii)	x,	y,	$1+z$				
a) High-temperature phase (298 K)							
I(1)–H(C2)	3.34(10)			I(2)–H(C2$^{\mathrm{i}}$)	3.24(7)		
I(2)–H(C8)	3.37(14)			I(2)–H(C4$^{\mathrm{ii}}$)	3.29(7)		
b) Low-temperature phase (110 K)							
I(1)–H(C3)	3.40(30)			I(1)–H(C14$^{\mathrm{ii}}$)	3.26(24)		
I(2)–H(C7)	3.39(33)			I(2)–H(C14$^{\mathrm{ii}}$)	3.18(21)		
I(2)–H(C8)	3.16(35)			I(3)–H(C19$^{\mathrm{ii}}$)	3.38(28)		
I(2)–H(C26a$^{\mathrm{iii}}$)	3.16(34)			I(1)–H(C1$^{\mathrm{vi}}$)	3.28(25)		
I(1)–H(C16$^{\mathrm{iv}}$)	3.31(30)			I(1)–H(C17$^{\mathrm{vi}}$)	3.29(28)		
I(3)–H(C20$^{\mathrm{iv}}$)	3.40(43)			I(2)–H(C6$^{\mathrm{vi}}$)	3.29(30)		
I(3)–H(C21$^{\mathrm{iv}}$)	3.35(37)			I(3)–H(C17$^{\mathrm{vi}}$)	3.10(20)		
I(3)–H(C13a$^{\mathrm{v}}$)	3.33(34)						

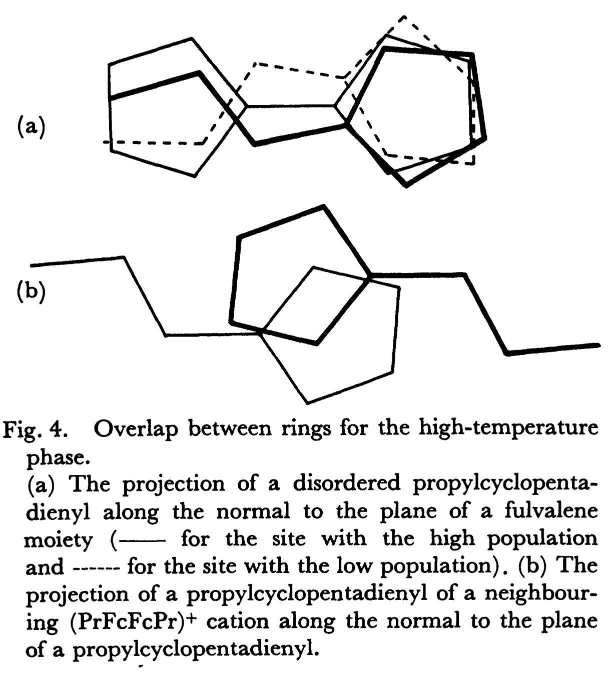

Fig. 4. Overlap between rings for the high-temperature phase.
(a) The projection of a disordered propylcyclopentadienyl along the normal to the plane of a fulvalene moiety (—— for the site with the high population and ------ for the site with the low population). (b) The projection of a propylcyclopentadienyl of a neighbouring (PrFcFcPr)$^+$ cation along the normal to the plane of a propylcyclopentadienyl.

and the fulvalene moiety in the high-temperature phase. The mean C–C bond distances in the inner and outer five-membered rings are 1.413(4) and 1.428(18) Å, respectively, and the outer ring shows larger thermal vibrations. This distance agrees with 1.425 Å observed in compound ferrocene at 169 K.[18] The C(5)–C(5′) bond distance in the fulvalene moiety is 1.46(2) Å.

Anion I_3^-: The triiodide anion is at the symmetry center, showing a symmetric structure. The I(1)–I(2) bond distance is 2.926(1) Å corresponding to 2.920 Å in free I_3^- ion.[23]

Low-temperature Phase (110 K): *Packing*: Figure 3(b) shows a packing view at 110 K. The structure is constructed by segregated columns of cation (PrFcFcPr)$^+$ and anion I_3^- similarly to that in the high-temperature phase. A three-dimensional hydrogen bond network is clearly found between the hydrogen atoms of a cation and the iodine atoms, in contrast to that at 298 K. Short contacts are found in the data given in Table 4. The interplanar distance of five-membered rings between neighboring cations is 3.40(4) Å, which is shorter by 0.07 Å than that at 298 K.

Structure of Cation (PrFcFcPr)$^+$: The symmetry center is lost and ferrocene- and ferrocenium-like units are crystallographically discernible in the cation. Their ring-ring distances are 3.28(4) and 3.41(5) Å for ferrocene- and ferrocenium-like units, respectively. These values are in agreement with 3.277(19) Å for the ferrocene-like unit and 3.397(22) Å for the ferrocenium-like unit in the trapped-valence cation diferrocenylselenium$^+$ [5] and 3.291—3.320 Å for three ferrocene-like units and 3.428 Å for a ferrocenium-like unit reported for ferricenyl(III) tris(ferrocenyl(II))borate.[24] The mean bond distances of Fe(2)–C and Fe(1)–C are 2.04(3) and 2.11(2) Å for the ferrocene- and ferrocenium-like units, respectively.

The rotational disorder of the propylcyclopentadienyl rings remains at 110 K but the population increases from 0.75(2) to 0.90(4) and 0.82(4) in the sites having the high population in the ferrocene- and ferrocenium-like units, respectively.

Anion I_3^-: The triiodide anion sits at the regular position at 298 K, whereas it exhibits a positional disorder with population ratio 0.90 : 0.10 at 110 K. When the propylcyclopentadienyl ring changes its position from the site with the low population to that with the high population, the propyl group ought to rotate around the C(10)–C(11) bond. As this rotation gives rise to a short contact between the propyl group and iodine atoms, the I_3^- anion seems to move away from the propyl group, and the I_3^- anion causes a positional disorder with population ratio 0.90 : 0.10. Bond distances of I(1)–I(2) and I(1)–I(3) are found to be 2.948(8) and 2.902(7) Å, respectively.

Infrared Spectroscopy. Infrared spectral data obtained at 294 and 78 K are shown in Table 7. No

Table 5. Bond distances and bond angles with e.s.d.'s in parentheses for the high-temperature phase (298 K)

(a) Bond distance	l/Å		l/Å
Fe–C(1)	2.043(7)	Fe–C(6)	2.062(19)
Fe–C(2)	2.037(9)	Fe–C(7)	2.042(22)
Fe–C(3)	2.030(11)	Fe–C(8)	2.038(28)
Fe–C(4)	2.041(11)	Fe–C(9)	2.103(13)
Fe–C(5)	2.083(10)	Fe–C(10)	2.116(17)
C(1)–C(2)	1.417(15)	C(6)–C(7)	1.457(35)
C(2)–C(3)	1.398(12)	C(7)–C(8)	1.398(27)
C(3)–C(4)	1.417(18)	C(8)–C(9)	1.483(41)
C(4)–C(5)	1.409(11)	C(9)–C(10)	1.395(30)
C(1)–C(5)	1.422(13)	C(6)–C(10)	1.408(33)
		C(10)–C(11)	1.522(33)
C(5)–C(5′)	1.458(21)	C(11)–C(12)	1.481(24)
		C(12)–C(13)	1.527(43)
(b) Bond angles	ϕ/°		ϕ/°
C(2)–C(1)–C(5)	107.7(8)	C(7)–C(6)–C(10)	113.0(16)
C(1)–C(2)–C(3)	108.9(10)	C(6)–C(7)–C(8)	100.2(18)
C(2)–C(3)–C(4)	107.2(9)	C(7)–C(8)–C(9)	114.5(23)
C(3)–C(4)–C(5)	109.1(8)	C(8)–C(9)–C(10)	103.3(19)
C(1)–C(5)–C(4)	107.1(8)	C(6)–C(10)–C(9)	108.6(22)
C(1)–C(5)–C(5′)	125.7(7)	C(6)–C(10)–C(11)	128.5(20)
C(4)–C(5)–C(5′)	127.2(8)	C(9)–C(10)–C(11)	122.9(18)
		C(10)–C(11)–C(12)	115.7(16)
		C(11)–C(12)–C(13)	111.1(19)

Table 6. Some least-squares planes and deviations (d/Å) of atoms from their planes in the high-temperature phase (298 K)

Equations of the least-squares planes refer to the orthogonal coordinate system defined by X along a Y in the ab plane, and Z along c^{*}. The atoms with asterisks were included in the calculations of the least-squares planes.

Plane(I) Fulvalene moiety $(0.1360X+0.3284Y-0.9347Z=0.5793)$			
C(1)*	0.013(9)	C(4)*	0.003(10)
C(2)*	−0.009(10)	C(5)*	−0.017(10)
C(3)*	0.006(10)	Fe	1.656(4)
Plane(II) Five-membered ring of propylcyclopentadienyl $(-0.2012X-0.2358Y+0.9507Z=2.6798)$			
C(6)*	0.021(22)	C(11)	−0.010(21)
C(7)*	−0.037(21)	C(12)	−0.098(23)
C(8)*	0.036(27)	C(13)	−0.120(31)
C(9)*	−0.021(20)	Fe	1.678(13)
C(10)*	−0.001(20)		
Plane(III) Four carbon atoms of propyl group $(-0.2146X-0.2921Y+0.9320Z=2.5975)$			
C(10)*	0.005(16)	C(12)*	−0.004(19)
C(11)*	−0.006(17)	C(13)*	0.005(28)
Dihedral angles (ϕ/°)			
Plane(I)–Plane(II)	6.6		
Plane(I)–Plane(III)	5.0		
Plane(II)–Plane(III)	3.5		

difference is found in the infrared spectral shapes for the two unoxidized compounds between 294 and 78 K, except for the narrowing of band width found at 78 K.

μ-(as-Indacenediyl)-bis(cyclopentadienyliron) System: Infrared spectra of the unoxidized molecule and mono-oxidized salt are illustrated in Fig. 5. The spectra of the mono-oxidized salt as well as the unoxidized molecule show no change at 294 and 78 K. A discernible difference between the infrared spectra of the unoxidized and mono-oxidized species is found in the band region from 400 to 500 cm^{-1} and in the bands in the vicinity of 800 cm^{-1}. By analogy with ferrocene,25) the 470 cm^{-1} band of the unoxidized molecule may be assigned to the asymmetric ring-metal-ring strech and the 485 cm^{-1} band to the asymmetric ring-metal-ring tilt. These bands are reduced in intensity in the mono-oxidized salt as compared with the unoxidized molecule. A similar tendency was also observed in the ferrocene system.26) The bands in the vicinity of 800 cm^{-1} can be assigned to the perpendicular CH bend. Although it was observed by means of Mössbauer spectroscopy that the mono-oxidized salt gradually undergoes a transition from an averaged-valence state of iron atoms to a trapped-valence state as temperature was lowered, infrared spectra of this salt is found to be temperature-independent. Supposing that the rate of electron transfer between two iron atoms is higher than the time scale of Mössbauer spectroscopy (*ca.* 10^{7} s^{-1}), is lower than that of infrared spectroscopy (*ca.* 10^{13} s^{-1}) at room temperature, and becomes lower than 10^{7} s^{-1} at 78 K, the results may be considered not to be in contradiction to the observation of line broadening at higher temperatures found in Mössbauer spectroscopy.9,10)

1′1‴-Diethyl- and 1′,1‴-Dipropylbiferrocene System: Infrared spectra of the mono-oxidized salts of diethyl- and dipropylbiferrocene are similar except for the band at 736 cm^{-1}, which appears in cation dipropylbiferroce-

TABLE 7. COMPARISON BETWEEN INFRARED SPECTRAL DATA AND MÖSSBAUER SPECTRAL DATA

Compound	Tmperature/K	Infrared spectra	Mössbauer spectra[9-11]
μ-(as-Indacenediyl)-bis-(cyclopentadienyliron)	294 78	No change	
1′,1‴-Diethylbiferrocene	294 78	No change	
μ-(as-Indacenyl)-bis(cyclopentadienyliron)$^+I_3^-$ 0.5 I_2	294 78	No change	Averaged-valence Trapped-valence
1′,1‴-Diethylbiferrocenium$^+I_3^-$	294 78	Remarkable change in intensity of bands at 680 and 1525 cm^{-1}	Averaged-valence Trapped-valence
1′,1‴-Dipropylbiferocenium$^+I_3^-$ (PrFcFcPr)$^+I_3^-$	294 78	Remarkable change in intensity of bands at 680 and 1525 cm^{-1}	Averaged-valence Trapped-valence

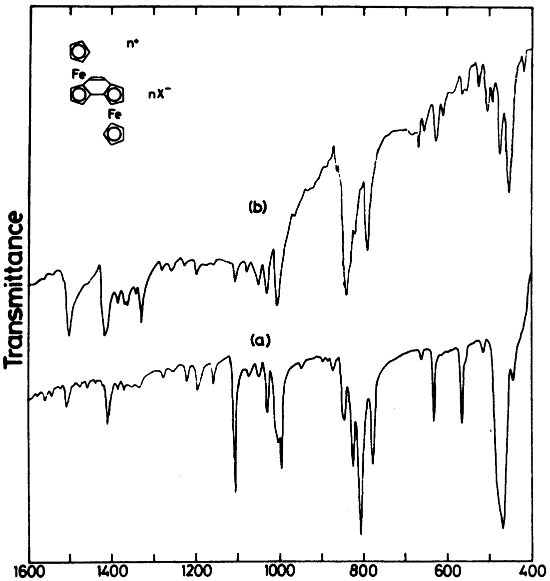

Fig. 5. Infrared spectra of KBr pellets of (a) μ-(as-indacenediyl)-bis(cyclopentadienyliron) at 294 K (n=0, X=none) and (b) μ-(as-indacenyl)-bis(cyclopentadienyliron)$^+I_3^-$ 0.5I_2 at 78 K (n=1, X=I_3^-0.5I_2).

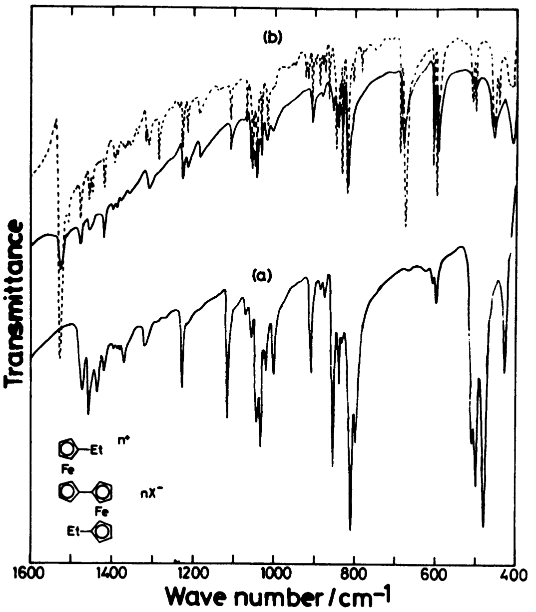

Fig. 6. Infrared spectra of KBr pellets of (a) 1′,1‴-diethylbiferrocene at 294 K (n=0, X=none) and (b) 1′,1‴-diethylbiferrocenium$^+I_3^-$ at 294 K (——) and 78 K (------) (n=1, X=I_3^-).

nium$^+$, attributable to the propyl group. Figure 6 shows spectra of diethylbiferrocene and its mono-oxidized salt. A discernible difference between these two species is observed in the band region from 400 to 500 cm^{-1} and in the bands around 800 cm^{-1}, similarly to the case of μ-(as-indacenediyl)-bis(cyclopentadienyliron) and its mono-oxidized cation. However, these bands change in the mono-oxidized salt, depending on temperature. It should be noted that new intense bands appear at 680 and 1525 cm^{-1} on going from the unoxidized molecule to the mono-oxidized salt. These bands are remarkably larger at 78 K than at 294 K. The band at 680 cm^{-1} seems to be assigned to the fulvalene moiety, because it is observed that a new band appears at 674 cm^{-1} in the biferricenylenium$^+PF_6^-$ salt with two fulvalene moieties.[6]

Conclusion

According to the results of infrared spectra and Mössbauer spectra,[11] the electrons in the (PrFcFcPr)$^+I_3^-$ salt are fully delocalized above the transition point (240 K), whereas below the transition temperature the salt has its electrons localized more in one Fc moiety than in the other. At 78 K, the electrons are almost localized and the ferrocene- and ferrocenium-like conformations become observable. The result of crystal structure suggests that a strong interaction within the cation is found between the propyl group and fulvalene moiety and the electrons get delocalized easily through the fulvalene moiety in consonance with this interaction, whereas at 110 K a three-dimensional hydrogen bond network is formed between the cation and iodine stoms, causing the interaction between the propyl group and fulvalene moiety to get weaker and the electrons to get localized. It was reported that the transition temperatures of 1′,1‴-diethylbiferrocenium$^+$-I_3^- and (PrFcFcPr)$^+I_3^-$ are 270 and 240 K, respectively. If the interaction between the substituent and fulvalene moiety brings about easier delocalization of electrons between the two iron atoms, the propyl group is expected to cause a stronger interaction than the ethyl group, and accordingly, to make the transition point from the averaged-valence state to the trapped-valence state lower in dipropyl- than in diethylbiferrocenium$^+$ cation.

The reason why the unsubstituted biferrocenium$^+$ cation is in a temperature-independent trapped-valence state, is also interpreted similarly by assuming an absence of this kind of interaction with the fulvalene ring. It should be mentioned that the interaction between the cation and the anion also has much to do with the electronic state of the cation.

In cation μ-(as-indacenyl)-bis(cyclopentadienyliron)$^+$, the electrons hop faster between the two iron atoms as temperature is raised. This indicates that the resonance energy is not large enough to delocalize the electrons between the two iron atoms.

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