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Neutral and Monocationic Dinuclear (Carbonyl)(cyclopentadienyl)(phenylchalcogenate) Iron Complexes of the General Formulas $[(RC_5H_4)Fe(CO)EPh]_2$ and $[(RC_5H_4)Fe(CO)EPh]_2PF_6$ (E = S or Te; R = H or Me): Synthesis, Molecular Structures, and EPR Spectra

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Abstract—Heating of the compounds $(RC_5H_4)Fe(CO)_2TePh$ (R = H (**I**) and Me (**II**)) in heptane afforded the dinuclear complexes $[(RC_5H_4)Fe(CO)TePh]_2$ (**III** and **IV**, respectively). By oxidation with $Fc^+PF_6^-$, these complexes were transformed into the paramagnetic cationic complexes $[(RC_5H_4)Fe(CO)TePh]_2PF_6$ (**V** and **VI**, respectively). Structures **III–V** and $[(C_5H_5)Fe(CO)SPh]_2PF_6$ (**VII**) were characterized by X-ray diffraction.

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INTRODUCTION

Transition metal chalcogenides are very attractive because of their optical and electrical properties [1, 2]. They have semiconducting to metallic conduction [3, 4] and exhibit interesting magnetic properties. In particular, iron diselenides and ditellurides, $FeSe_2$ and $FeTe_2$, with pyrite- or marcasite-like structures are magnetically ordered in the crystalline state [5]. Recently, it has been discovered that the superconductivity temperature of FeSe in the crystal structure of PbO is 8 K [6] and that iron tellurides in which the Te atoms are partially replaced by selenium or sulfur, $FeTe_{1-x}(Se,S)_x$, have a superconductivity temperature of 15 K [7].

Organoiron chalcogenide complexes like the well-known dimeric complex $[(C_5H_5)Fe(CO)SPh]_2$ (Fe···Fe 3.39 Å) [8] can be regarded as possible precursors of such inorganic materials. The above dimer readily undergoes one-electron oxidation to the radical cation $[(C_5H_5)Fe(CO)SPh]_2^{+\bullet}$, which can be isolated with the anion BPh_4^- [9] or the radical anion $TCNQ^{-\bullet}$ [10] and has a one-electron Fe---Fe bond (2.95 Å). The resulting paramagnetism of the complex can be detected by EPR spectroscopy. It appeared interesting to obtain phenyltellanyl analogs of the neutral and monocationic dimers and examine their structural characteristics and EPR spectra of monocations.

EXPERIMENTAL

All reactions were carried out under argon in dehydrated solvents using standard Schlenk ware. The course of the reactions was monitored by TLC and IR spectroscopy. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer. Elemental analysis was performed on a Carlo Erba CHNS analyzer. X-ray diffraction was studied on a Bruker APEX II CCD diffractometer. The EPR spectra of compounds **V** and **VI** in acetonitrile and in the polycrystalline state were recorded on a ELEXSYS E-680 X spectrometer (Bruker) at 293 and 77 K.

The starting complexes $(C_5H_5)_2FePF_6$ [11, p. 1958], $[C_5H_5Fe(CO)_2]_2$, $[C_5H_4CH_3Fe(CO)_2]_2$ [11, p. 1983], $(C_5H_5Fe(CO)_2TePh$ (**I**)), and $(C_5H_4CH_3Fe(CO)_2TePh$ (**II**)) [12] were prepared as described earlier.

Synthesis of $[C_5H_5Fe(CO)TePh]_2$ (III). A red-brown solution of $[C_5H_5Fe(CO)_2]_2$ (0.30 g, 0.85 mmol) and diphenyl ditelluride (0.35 g, 0.85 mmol) in benzene (30 mL) in a quartz Schlenk vessel was exposed to UV light for 3 h while cooling it with running water. The resulting brown solution was concentrated and the residue was recrystallized from boiling heptane. The yield of complex **III** was 0.28 g (46%), black-brown crystals.

For $C_{24}H_{20}Fe_2O_2Te_2$ (M = 707.31)		
anal. calcd., %:	C, 40.75;	H, 2.85.
Found, %:	C, 41.34;	H, 2.90.

IR (KBr; ν, cm^{-1}): 3442 m.br, 3052 w, 1913 vs (CO), 1895 vs (CO), 1633 w, 1571 w, 1471 w, 1432 w, 1111 w, 1062 w, 1016 w, 998 w, 840 w, 809 w, 733 w, 692 w, 573 w, 554 w, 540 w, 455 w.

Synthesis of [$C_5H_4CH_3Fe(CO)TePh]_2$ (IV). A red-brown solution of [$C_5H_4CH_3Fe(CO)_2]_2$ (0.30 g, 0.785 mmol) and diphenyl ditelluride (0.32 g, 0.785 mmol) in benzene (12 mL) was stirred at 70–75°C for 7 h and then evaporated to dryness. The residue was refluxed in heptane (15 mL) for 6 h. The resulting brown solution was filtered and cooled. The brown crystals that formed were separated, washed with cold heptane (5 mL), and dried in vacuo. The yield of complex **IV** was 0.25 g (43%).

For $C_{26}H_{24}Fe_2O_2Te_2$ (M = 735.36)		
anal. calcd., %:	C, 42.46;	H, 3.28.
Found, %:	C, 43.14;	H, 3.26.

IR (KBr; ν, cm^{-1}): 3796 vw, 3466 m.br, 3119 vw, 3183 vw, 3060 vw, 3049 w, 2951 vw, 2918 w, 2850 vw, 1932 vs (CO), 1899 vs (CO), 1603 vw, 1570 m, 1472 m, 1453 vw, 1433 m, 1371 vw, 1324 vw, 1297 w, 1269 vw, 1235 vw, 1175 vw, 1156 vw, 1113 w, 1062 w, 1032 vw, 1017 w, 997 w, 924 w, 834 m, 733 m, 692 w, 555 w, 545 w, 536 w, 458 w.

Synthesis of [$C_5H_5Fe(CO)TePh]_2^+PF_6^-$ (V). Complex **III** (0.27 g, 0.38 mmol) was dissolved in acetone (7.5 mL). A solution of $Fc^+PF_6^-$ (0.12 g, 0.38 mmol) in acetone (7.5 mL) was slowly added with stirring for 40 min. The resulting solution was stirred for 10 min and concentrated. The brown solid residue was washed with heptane (15 mL). Organic materials were extracted with CH_3CN (5 mL), giving a brown solution and a green precipitate. The precipitate was filtered off, recrystallized from CH_3CN (15 mL), and dried in vacuo. The yield of complex **V** was 0.03 g (10%).

For $C_{24}H_{20}F_6Fe_2O_2PTe_2$ (M = 852.28)		
anal. calcd., %:	C, 33.82;	H, 2.37.
Found, %:	C, 34.23;	H, 2.34.

IR (KBr; ν, cm^{-1}): 3107 w, 3048 vw, 1982 vs (CO), 1964 vs (CO), 1927 m (CO), 1570 m, 1475 w, 1460 w, 1435 m, 1426 m, 1417 m, 1357 w, 1311 w, 1181 w, 1112 w, 1059 w, 1015 m, 999 m, 948 vw, 934 vw, 876 s, 863 s, 835 vs, 826 vs, 751 s, 694 m, 662 vw, 651 w, 595 w, 557 s, 532 s, 463 m.

Synthesis of [$(C_5H_4CH_3)Fe(CO)TePh]_2^+PF_6^-$ (VI). A solution of $Fc^+PF_6^-$ (0.081 g, 0.245 mmol) in acetone (5 mL) was added dropwise for 20 min to a stirred solution of complex **IV** (0.18 g, 0.245 mmol) in acetone (5 mL). The resulting mixture was stirred for 10 min and concentrated in a water aspirator vacuum. The residue was washed with diethyl ether (2 × 15 mL). The dark green solid residue was recrystallized from MeCN (10 mL) with addition of diethyl ether. The yield of complex **VI** was 0.083 g (38%).

For $C_{26}H_{24}F_6Fe_2O_2PTe_2$ (M = 880.33)		
anal. calcd., %:	C, 35.47,	H, 2.74.
Found, %:	C, 35.11,	H, 2.36.

IR (KBr; ν, cm^{-1}): 3449 w.br, 3112 w, 3093 w, 1977 vs (CO), 1960 m (CO), 1924 vw (CO), 1570 w, 1479 w, 1455 w, 1434 w, 1388 vw, 1060 w, 1027 w, 1015 vw, 997 vw, 863 m, 838 vs, 749 m, 694 w, 555 m, 530 m, 460 w.

Synthesis of [$C_5H_5Fe(CO)SPh]_2^+PF_6^- \cdot CH_3CN$ (VII). Dichloromethane (11 mL) was added to a mixture of [$C_5H_5Fe(CO)SPh]_2$ (0.30 g, 0.58 mmol) and $Fc^+PF_6^-$ (0.19 g, 0.58 mmol). The resulting brown solution was stirred for 1.5 h, which caused it to turn green. The solution was evaporated to dryness in vacuo. The residue was washed with heptane (2 × 10 mL) and recrystallized from CH_3CN (20 mL). The yield of complex **VII** was 0.17 g (42.3%), black-green crystals.

For $C_{26}H_{23}F_6Fe_2NO_2PS_2$ (M = 702.25)		
anal. calcd., %:	C, 44.47;	H, 3.30.
Found, %:	C, 43.71;	H, 2.58.

IR (KBr; ν, cm^{-1}): 3937 w, 3451 m.br, 3119 m, 3063 w, 2540 w, 2293 w, 2258 w, 2015 vs (CO), 1998 vs (CO), 1972 s (CO), 1841 w, 1632 w, 1577 m, 1470 m, 1438 m, 1431 m, 1419 m, 1359 w, 1308 w, 1274 w, 1177 w, 1158 w, 1117 w, 1073 w, 1064 w, 1041 w, 1022 w, 1016 w, 1000 w, 975 w, 958 w, 924 w, 877 s, 836 vs, 752 s, 697 m, 617 w, 589 w, 558, 536 s, 486 m.

X-ray diffraction study. Crystallographic parameters and the data collection and refinement statistics for structures **III–V** and **VII** are given in table. Absorption correction was applied by multiple measurements of equivalent reflections with the SADABS program [13]. Structures **III–V** and **VII** were solved by the direct methods and refined anisotropically for the non-hydrogen but C atoms by the least-squares method on F^2 with the SHELXTL program package [14]. The hydrogen atoms were located geometrically. Selected bond lengths and bond angles in structures **III–V** and **VII** are given in the captions to Figs. 1–4.

Atomic coordinates and other parameters for structures **III–V** and **VII** have been deposited with the Cambridge Crystallographic Data Centre (nos. 941700, 941701, 941702, and 941703 for complexes **V**, **VII**, **III**, and **IV**, respectively; http://www.ccdc.cam.ac.uk/data_request/cif).

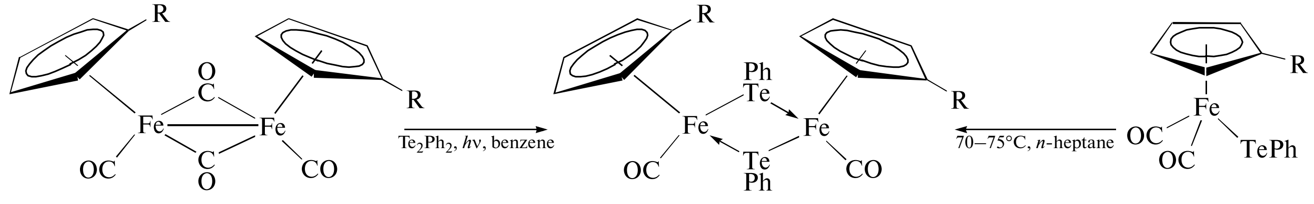
Crystallographic parameters and the data collection and refinement statistics for complexes **III–V** and **VII**

Parameter	Value			
	III	**IV**	**V**	**VII**
M	707.30	735.35	852.27	702.24
Diffractometer	Bruker APEX II CCD			
Radiation (λ, Å)	MoK_α (0.71073)			
Temperature, K	296(2)			
Space group	*Pbca*	$P2_1/c$	$C2$	$P\bar{1}$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
a, Å	13.343(3)	19.549(2)	17.632(4)	10.187(3)
b, Å	17.279(3)	8.1147(9)	8.030(2)	10.408(3)
c, Å	20.156(4)	16.7144(9)	12.584(3)	15.091(6)
α, deg	90	90	90	108.017(5)
β, deg	90	111.738(2)	133.291(3)	101.070(5)
γ, deg	90	90	90	102.896(4)
V, Å^3	4647.0(16)	2463.0(5)	1297.0(5)	1423.1(8)
Z	8	4	2	1
ρ_{calcd}, g/cm^{-3}	2.022	1.983	2.182	1.639
μ, mm^{-1}	3.728	3.521	3.450	1.287
$F(000)$	2688	1408	810	710
θ scan range, deg	2.18–29.00	1.12–29.00	2.22–26.46	1.48–29.13
Scan mode	ω			
Number of unique reflections (N_1)	6178 ($R_{\text{int}} = 0.0375$)	6485 ($R_{\text{int}} = 0.0251$)	2646 ($R_{\text{int}} = 0.0161$)	7590 ($R_{\text{int}} = 0.0169$)
Number of reflections with $I > 2\sigma(I)$ (N_2)	4732	5543	2529	6286
Number of parameters refined	271	289	169	357
GOOF (F^2)	1.081	1.025	1.066	1.023
R_1 for N_2	0.0285	0.0271	0.0167	0.0358
wR_2 for N_1	0.0673	0.0677	0.0410	0.1045
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	1.020/–0.511	1.252/–0.448	0.538/–0.376	0.632/–0.424

RESULTS AND DISCUSSION

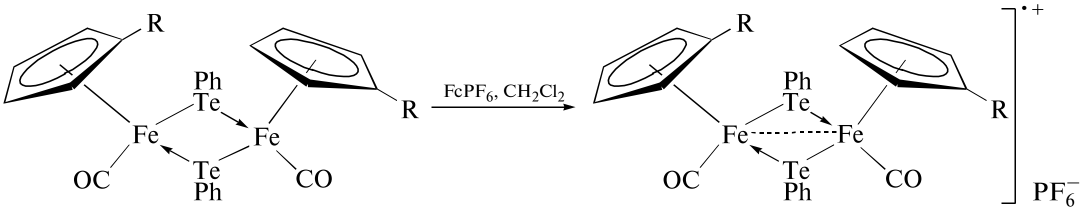
Reflux of the green mononuclear complexes **I** and **II** (initially formed in photochemical or thermal reactions of $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_4CH_3Fe(CO)_2]_2$ with diphenyl ditelluride) in heptane results in elimination of one CO group and formation of brown dimers **III** and **IV**; their crystals are suitable for X-ray diffraction (Figs. 1, 2). The phenyl and cyclopentadienyl groups are opposite in pairs to each other relative to the Fe_2Te_2 ring. Complexes **III** and **IV** can be classified as (*trans*-Cp, *anti*-R)-$[(C_5H_5)Fe(CO)TePh]_2$ [15]. Complex **III** shows no bond between the iron atoms; the Fe–Te bonds (2.5491(7) and 2.5700(6) Å) are substantially shorter than the sum of the covalent radii of these atoms ($r_{Fe} + r_{Te} = 2.70$ Å [16]). This suggests their partial double character, probably because of an additional dative interaction of the lone electron pair on the Fe atom with the vacant *d* orbitals of tellurium [17]. The IR spectrum of this complex contains two bands at 1913 (vs) and 1895 cm^{-1} (vs) due to the CO stretching vibrations; TLC revealed a light brown spot ($R_f = 0.51$) that turns green when exposed to air.

Dimeric complex **IV** containing the methylcyclopentadienyl ligands was obtained by heating $[(MeC_5H_4)Fe(CO)_2]_2$ with diphenyl ditelluride in heptane. The IR spectrum of complex **IV** shows two bands at 1932 (vs) and 1899 cm^{-1} (vs) due to the CO stretching vibrations. According to X-ray diffraction data, this complex has the same structure as (*trans*-Cp, *anti*-R)-$[(C_5H_5)Fe(CO)TePh]_2$. As in complex **III**, the Fe–Te bonds in complex **IV** are strongly shortened (2.5663(5), 2.5497(6), 2.5446(5), and 2.5687(6) Å).



R = H (**III**), Me (**IV**)

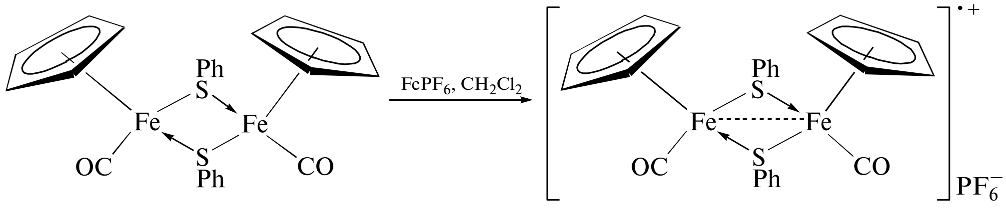
The brown dimers **III** and **IV** were oxidized with $Fc^+PF_6^-$ in CH_2Cl_2 to give green paramagnetic cationic complexes **V** and **VI**.



R = H (**V**), Me (**VI**)

The IR spectra of these complexes contain two intense bands at 1982 and 1964 cm^{-1} (for R = H) and at 1977 and 1959 cm^{-1} (R = Me) due to the CO stretching vibrations. According to the X-ray diffraction data, the CO groups and the phenyl rings in complex **V** (Fig. 3) are on the same side of the plane of the Fe_2Te_2 ring, thus forming a (*cis*-Cp, *syn*-R) isomer. The Fe–Fe bond in structure **V** (3.3217(9) Å) is substantially shorter than the corresponding Fe···Fe distance in the neutral complex (3.745 Å); however, it is longer than the double covalent radius of the iron atom ($2r_{Fe}$ = 2.64 Å [16]). This agrees with the formation of a one-electron bond between metal atoms. The Fe–Te bonds are also shortened (2.5229(8) and 2.5367(8) Å) because of positive charges on the iron atoms.

Oxidation of the brown thiolate-bridged complex $[(C_5H_5)Fe(CO)SPh]_2$ with $FcPF_6$ in CH_2Cl_2 also gives the green paramagnetic cationic complex $[(C_5H_5)Fe(CO)SPh]_2PF_6$ (**VII**), which is similar to a known complex with the tetraphenylborate anion [9].



The IR spectrum of complex **VII** shows two bands at 2015 (vs) and 1998 cm^{-1} (vs) due to the CO stretching vibrations. These bands are shifted to the higher frequencies relative to those in the IR spectrum of the starting neutral dimer (1974 cm^{-1}, vs). Crystals suitable for X-ray diffraction were obtained by cooling a solution of complex **VII** in MeCN to –20°C.

According to X-ray diffraction data for complex **VII** (Fig. 4), the Fe atoms in the dinuclear cation are linked by two bridging SPh groups. In structure **VII**, all the four constituent atoms of the Fe_2S_2 ring are coplanar. As in the starting neutral dimer $[(C_5H_5)Fe(CO)SPh]_2$, the phenyl rings are *syn* to each other and *trans* to the cyclopentadienyl ligands; so this complex can be classified as a (*cis*-Cp, *syn*-R) isomer. The Fe–S bond lengths in complex **VII** are 2.2493(11), 2.2523(7), and 2.2502(10) Å. They are shorter than the sum of the covalent radii ($r_{Fe} + r_S$ = 2.37 Å [16]). The one-electron Fe---Fe bond length is 2.9396(7) Å; this value is greater than the double covalent radius of the iron atom (2.64 Å) but is substantially smaller than the corresponding Fe···Fe distance in the neutral complex (3.39 Å [8]).

The presence of an unpaired electron in complex **V** and **VI** was detected by EPR spectroscopy. The EPR spectrum of complex **V** in acetonitrile solution shows a singlet with g_{iso} = 2.1206. A similar signal is observed in the EPR spectrum of complex **VI** in CH_2Cl_2 (g_{iso} = 2.1440). The EPR spectra of powdered samples of these complexes can be described by the anisotropic

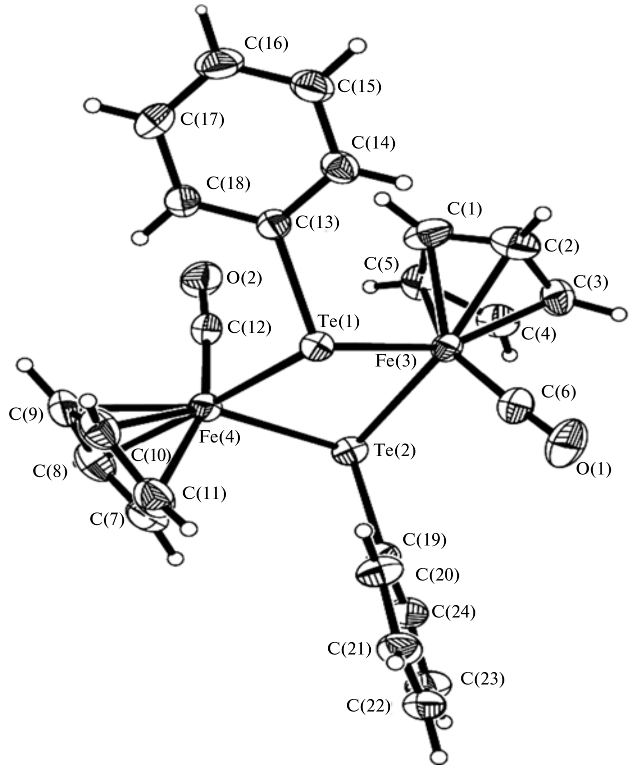


Fig. 1. Molecular structure of complex **III**. Selected distances: Fe(3)–Te(1), 2.5700(6) Å; Fe(3)–Te(2), 2.5491(7) Å; Fe(3)···Fe(4), 3.7452(9) Å.

spin Hamiltonian with a biaxial orientation of the g tensor: $g_{||} = 2.3416$, $g_{\perp} = 2.0227$ (**V**) and $g_{||} = 2.3214$, $g_{\perp} = 2.0092$ (**VI**). It should be noted that the anisotropy of the signals in the EPR spectra of complexes **V** and **VI** containing a heavy Te atom is much greater than that of the EPR signals for the corresponding sulfur analogs [9].

Thus, dinuclear cyclopentadienylcarbonyl iron complexes with two phenyltellanyl bridges are stereochemically flexible, giving a (*trans*-Cp, *anti*-R) isomer in a photochemical reaction in heptane. The IR spectrum of this isomer shows two bands due to the CO stretching vibrations. Oxidation of the dimers affords only dinuclear monocations with the (*cis*-Cp, *syn*-R)-configuration. Such a symmetry favors the formation of a one-electron Fe---Fe bond. This agrees with the geometry of the known dicationic complex $[(C_5H_5)Fe(CO)SEt]_2(PF_6)_2$ having the same (*cis*-Cp, *syn*-R)-configuration but a short single Fe–Fe bond (2.6444(10) Å [18]).

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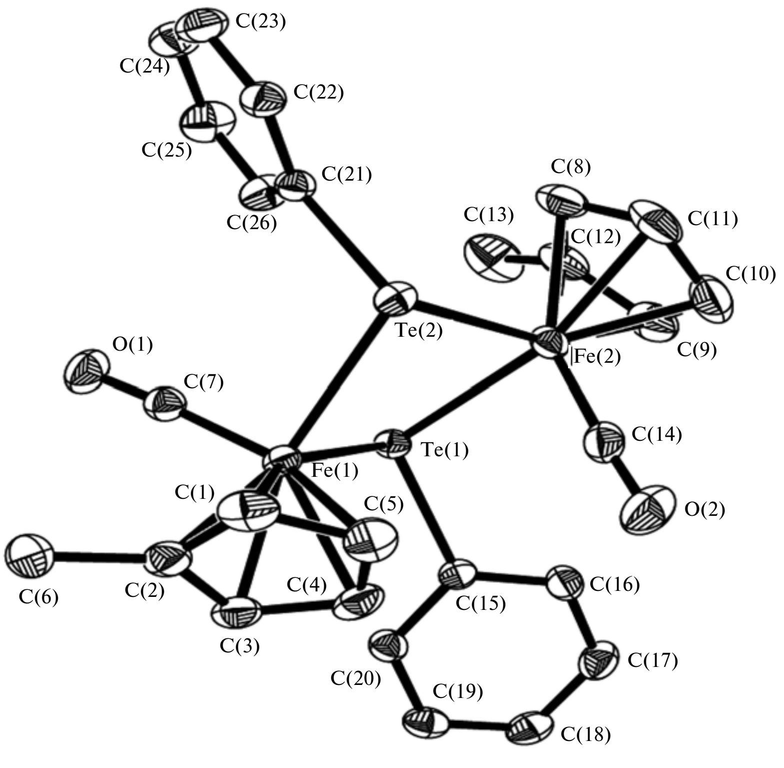

Fig. 2. Molecular structure of complex **IV**. Selected bond lengths: Fe(1)–Te(1), 2.5663(5) Å; Fe(1)–Te(2), 2.5497(6) Å.

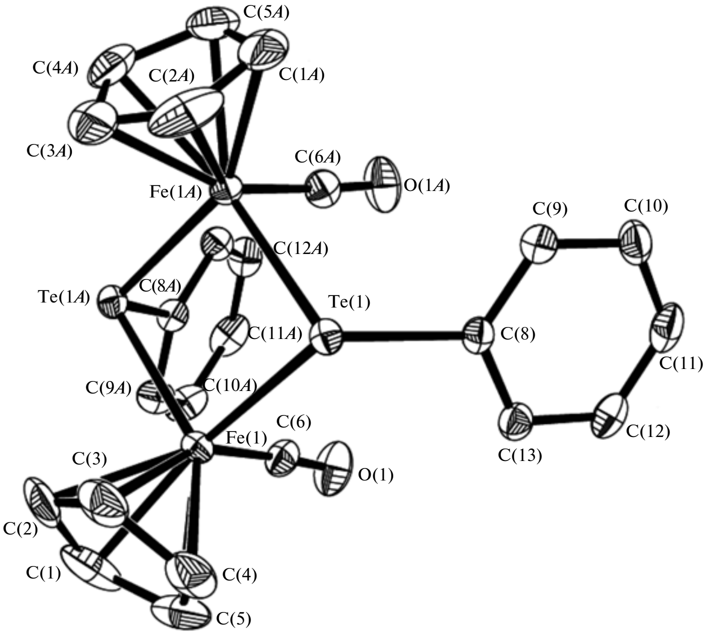

Fig. 3. Molecular structure of complex **V** (the hydrogen atoms are omitted for clarity). Selected bond lengths: Fe(1)---Fe(2), 3.3217(9) Å; Te–Fe, 2.5229(8) and 2.5367(8) Å.

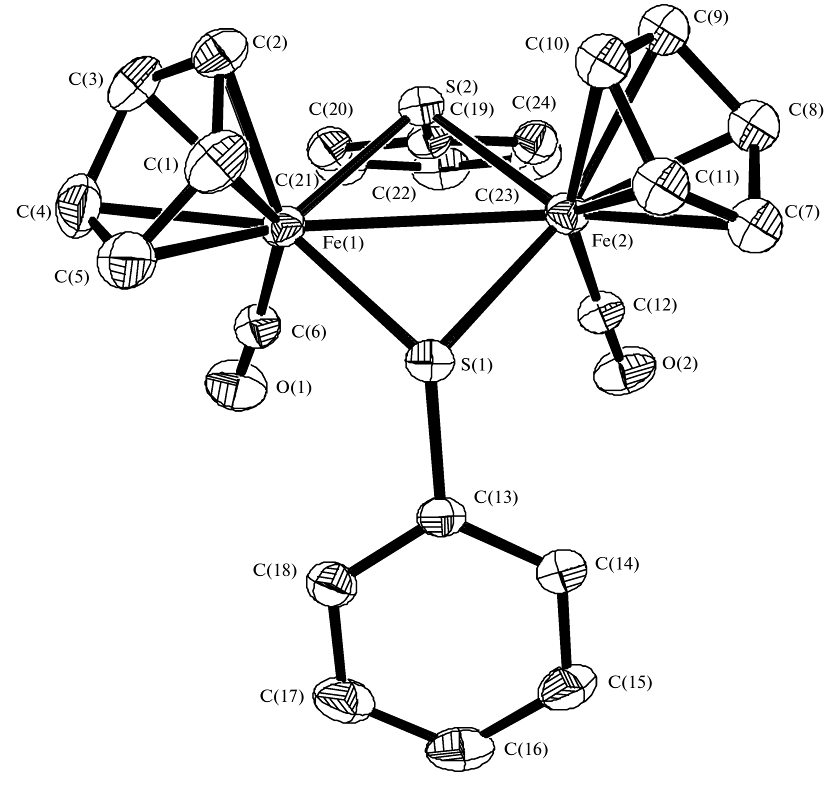

Fig. 4. Molecular structure of complex **VII** (the hydrogen atoms are omitted for clarity). Selected bond lengths: Fe(1)---Fe(2), 2.9396(7) Å; Fe(1)–S(1), 2.2493(11) Å; Fe(1)–S(2), 2.2523(7) Å; Fe(2)–S(2), 2.2502(10) Å.

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