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Oxidation of Ferrocene and 1,1'-Ferrocene Triselenide by Bromine and Phenyltellurium Tribromide

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Abstract—The reaction of 1,1'-ferrocene triselenide, $Fe(C_5H_4)_2Se_3$ (**I**), with bromine or phenyltellurium tribromide, $PhTeBr_3$, involves the oxidation of compound **I** to form salts $[Fe(C_5H_4)_2Se_3]^+FeBr_4^-$ (**II**) and $[Fe(C_5H_4)_2Se_3]^+PhTeBr_4^-$ (**III**), respectively. Depending on the crystallization conditions, the reaction of ferrocene with $PhTeBr_3$ affords salt $[Fc]^+[PhTeBr_4]^-$ (**IVa**), its solvate with benzene$\{[Fc]^+[PhTeBr_4]^-\}_2 \cdot C_6H_6$ (**IVb**), or etherate $[Fc]^+[Ph_2Te_2Br_6OH]^- \cdot 0.5(C_2H_5)_2O$ (**V**). The structures of compounds **II**, **III**, **IVa**, **IVb**, and **V** are determined by X-ray diffraction analysis (CIF files CCDC 1054193 (**II**), 1054192 (**III**), 1054194 (**IVa**), 1054195 (**IVb**), and 1054196 (**V**)).

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INTRODUCTION

Polychalcogenide ferrocene derivatives of the 1,2,3-trichalcogen-[3]ferrocenophane type, $Fe(C_5H_4)_2X_3$ (X = S or Se), obtained by the lithiation of ferrocene in the presence of tetramethylethylenediamine (TMEDA) followed by the treatment with chalcogen [1] contain the ferrocene ring capable of one-electron reversible oxidizing, for example, by tetracyanoquinodimethane (TCNQ) and halogens (in the case of the octamethylferrocenyl analog) [2] and of forming semiconducting paramagnetic salts with charge transfer to complexes $M(Mnt)_2$ (M = Ni, Co, Pt; Mnt is maleonitrile dithiolate) [3, 4].

According to the X-ray diffraction data, triselenide $Fe(C_5H_4)_2Se_3$ (**I**) contains no Fe...Se bonds (3.545, 3.823, 3.569 Å) and contain almost equalized Se–Se bonds, whose length (2.332 Å) [5] is close to that found in diphenyldiselenium, Ph_2Se_2 (2.307(1) Å) [6]. In the latter, this bond is not cleaved under the action of halogens and forms only charge-transfer complexes, $Ph_2Se_2 \cdot X_2$ (X = Br or I) [7]. Therefore, it seemed interesting to study the halogenation of compound **I** by bromine or phenyltellurium tribromide, $PhTeBr_3$.

EXPERIMENTAL

All procedures on the synthesis and isolation of compounds were carried out under an argon atmosphere in absolute solvents using standard Schlenk glassware. Commercial ferrocene, *tert*-butyllithium, TMEDA, selenium, and bromine were used without additional purification. Compound **I** was synthesized using a known procedure [1]. A CHNS analyzer (Carlo Erba) was used for chemical analysis. IR spectra were recorded in KBr pellets and in solutions of absolute organic solvents with compensation on a BrukerAlpha FT-IR spectrometer.

Synthesis of $[FcSe_3^+][FeBr_4^-]$ (II). Bromine (0.006 mL, 0.118 mmol) was added to a red solution of $FcSe_3$ (0.05 g, 0.118 mmol) in CH_2Cl_2 (7 mL) in an argon flow with magnetic stirring, and a small amount of a red precipitate was formed. Another portion of Br_2 (0.006 mL, 0.118 mmol) was added, and the red precipitate was dissolved. Red crystals suitable for X-ray diffraction began to form on the flask walls in 5 min. The crystals were decanted, washed with heptane (5 mL), and dried in vacuo. The yield was 0.05 g (46% based on $FcSe_3$).

Synthesis of $[FcSe_3^+][PhTeBr_4^-]$ (III). A red transparent solution of $FcSe_3$ (0.05 g, 0.118 mmol) in CH_2Cl_2 (0.5 mL) was placed in an ampule 5 mm in diameter and covered with a yellow solution of $PhTeBr_3$ (0.05 g, 0.112 mmol) in THF (0.5 mL). The ampule was closed and left to stay at room temperature. Red prismatic crystals of compound **III** suitable for X-ray diffraction analysis were formed at the interface of the solutions in 4 days.

Synthesis of $[Fc^+][PhTeBr_4^-]$ (IVa). An orange solution of FcH (0.019 g, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was placed in an ampule 5 mm in diameter and covered with several THF droplets and a yellow solution of $PhTeBr_3$ (0.05 g, ~0.112 mmol) in THF (0.5 mL). The ampule was closed and left to stay at room temperature. Dark green prismatic crystals of compound **IVa** suitable for X-ray diffraction analysis were formed in 2 days at the interface of the solutions.

Synthesis of [Fc^+][$PhTeBr_4^-$] · (C_6H_6) (IVb). An orange solution of FcH (0.019 g, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was placed in an ampule 5 mm in diameter and covered with several benzene droplets and a yellow solution of $PhTeBr_3$ (0.05 g, ~0.112 mmol) in THF (0.5 mL). The ampule was closed and left to stay at room temperature. Dark green prismatic crystals of compound **IVb** suitable for X-ray diffraction analysis were formed in 2 days at the interface of the solutions.

Synthesis of [Fc^+][$Ph_2Te_2Br_6OH$]$^-$ · $(C_2H_5)_2O$ (V). An orange solution of FcH (0.019 g, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was placed in an ampule 5 mm in diameter and covered with several ether droplets and a yellow solution of $PhTeBr_3$ (0.05 g, ~0.112 mmol) in THF (0.5 mL). The ampule was closed and left to stay at room temperature. Dark green prismatic crystals of compound **V** suitable for X-ray diffraction analysis were formed in 2 days at the interface of the solutions.

The **X-ray diffraction analyses** of single crystals of compounds **II–IV** were carried out on a Bruker APEX II CCD four-circle automated diffractometer. The crystallographic data and the refinement parameters for structures **II–V** are presented in the table. The calculations were performed using the SHELXTL program package [8]. An absorption correction was applied by the multiple measurements of equivalent reflections using the SADABS program [9]. Structures **II–V** were solved by a direct method. All non-hydrogen atoms were refined by the least-squares method relative to F^2 in the anisotropic approximation (SHELX-2014) [10]. The coordinates of the disordered atoms of the phenyl groups in structure **III** in the isotropic approximation with constraints imposed on the equality of typical distances (SAME instruction). The positions of hydrogen atoms were calculated geometrically. The structures of compounds **I–V** are shown in Figs. 1–5, and selected bond lengths and bond angles in the structures are given in the figure captions.

The coordinates of atoms and other parameters for structures **II–V** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1054193 (**II**), 1054192 (**III**), 1054194 (**IVa**), 1054195 (**IVb**), and 1054196 (**V**), respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

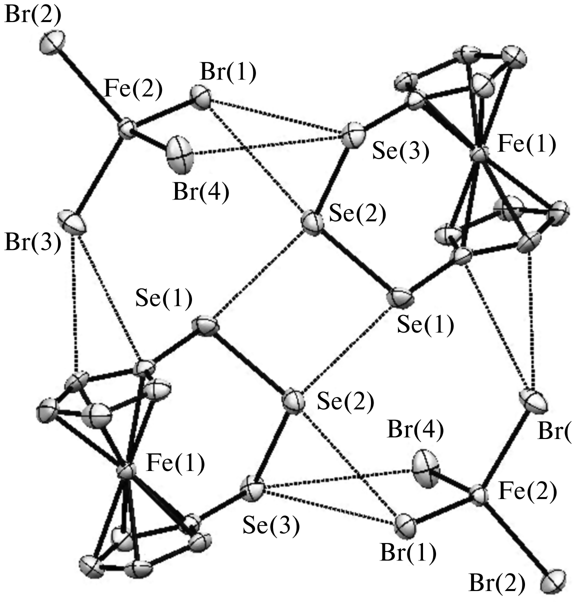
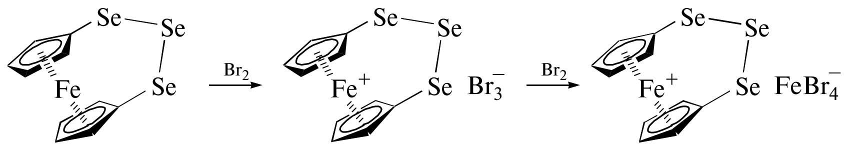


Fig. 1. Molecular structure of compound **II**. Main bond lengths (Se(2)–Se(1) 2.3367(4) and Se(3)–Se(2) 2.3347(4) Å) and intermolecular contacts (Se(2)–Se(1) 3.8357(4), Br(1)–Se(2) 3.5277(4), Br(1)–Se(3) 3.9336(4), Se(3)–Br(4) 3.7795(5), Br(1)–Se(2) 3.5277(4), Br(3)–C(5) 3.519(3), and Br(3)–C(1) 3.468(2) Å). Hydrogen atoms are omitted.

RESULTS AND DISCUSSION

The reaction of triselenide **I** with bromine in dichloromethane proceeds, most likely, in two stages to form first (at equimolar amounts of the reactants) a red precipitate, being probably salt $[FcSe_3]^+[Br_3]^-$, by analogy to the reaction of octamethyl derivative **I**. The latter (earlier obtained by the action of 1.5 moles of bromine) was better soluble due to the presence of methyl groups in the rings [2]. In our case, the red precipitate was dissolved upon the addition of one more mole of bromine, and red crystals of salt **II** were formed soon, evidently, due to the partial cleavage of the ferrocene ring



Crystallographic data and the experimental and refinement parameters for structures **II**–**V**

Parameter	Value				
	II	**III**	**IVa**	**IVb**	**V**
Empirical formula	$C_{16}H_{13}Se_3Br_4FeTe$	$C_{10}H_8Se_3Br_4Fe_2$	$C_{16}H_{15}Br_4FeTe$	$C_{19}H_{18}Br_4FeTe$	$C_{24}H_{26}Br_6FeO_{1..5}Te_2$
FW	696.46	740.53	597.54	749.42	1129.94
Temperature, K	293(2)	293(2)	296(2)	296(2)	173(2)
Radiation (λ, Å)	MoK_α (0.71073)				
Space group	*Pnma*	$P2_1/n$	$P2_1/n$	$P\bar{1}$	*C*2
a, Å	19.368(4)	12.1384(3)	10.433(2)	9.2196(5)	13.8695(19)
b, Å	13.099(3)	7.8753(2)	16.490(4)	15.0198(8)	11.0756(15)
c, Å	8.7074(19)	19.2980(5)	11.706(3)	17.2131(9)	13.0137(18)
α, deg	90	90	90	69.3120(10)	90
β, deg	90	100.434(2)	105.899(4)	75.4240(10)	114.959(2)
γ, deg	90	90	90	75.6100(10)	90
V, Å^3	2209.1(8)	1814.26(8)	1936.9(7)	2124.3(2)	1812.4(4)
Z	4	4	4	4	4
ρ_{calcd}, g/cm^{-3}	2.094	2.711	2.049	2.343	2.072
μ, mm^{-1}	8.882	15.641	5.901	9.580	8.626
F(000)	1284	1344	1108	1400	1040
θ range, deg	2.103–27.995	2.97–29.00	2.320–27.999	1.286–28.999	1.726–28.994
Scan type	w				
Total number of reflections	14096	17926	18122	23049	6526
Independent reflections (N_1)	2746 (R_{int} = 0.0550)	4821 (R_{int} = 0.0321)	4662 (R_{int} = 0.1362)	11190 (R_{int} = 0.0412)	3952 (R_{int} = 0.0415)
Reflections with $I > 2\sigma(I)$ (N_2)	2186	4100	2306	7735	5602
Number of refined parameters	119	172	199	559	173
Goodness-of-fit (F^2)	1.139	0.952	0.950	0.879	0.999
R_1 for N_2	$R_1 = 0.0638$	$R_1 = 0.0227$	$R_1 = 0.0546$	$R_1 = 0.0342$	$R_1 = 0.0417$
wR_2 for N_1	$wR_2 = 0.1626$	$wR_2 = 0.0426$	$wR_2 = 0.1187$	$wR_2 = 0.1020$	$wR_2 = 0.1039$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.398/–1.888	0.854/–0.645	1.004/–0.894	1.212/–1.129	1.638/–1.261

A similar destruction was observed earlier for ferrocene bromination with the formation of $Cp_2Fe^+FeBr_4^-$ [11], which can also been obtained from ferrocene and iron tribromide [12].

The structure of compound **II** was established by X-ray diffraction analysis. The Se–Se bond lengths in the cation remained nearly unchanged in structure **II** compared to the initial neutral compound **I** (2.332 Å). However, weak intermolecular Se–Se contacts (3.835 Å) appeared, as well as Se–Br (3.527–3.933 Å) involving the $FeBr_4^-$. anion. The Fe(1)–$Cp_{centroid}$ distance (1.710 Å) is typical of the ferricinium cation.

Note that the oxidation of Se(II) is impeded, unlike the known easy oxidation of Te(II) to Te(IV) [13]. For example, the bromination of the selenium-bridged dibromocyclooctane derivative, $(C_8H_{12})Br_2Se$ obtained by the addition of $SeBr_2$ to COD at both double bonds, proceeded without Br–Br bond cleavage.

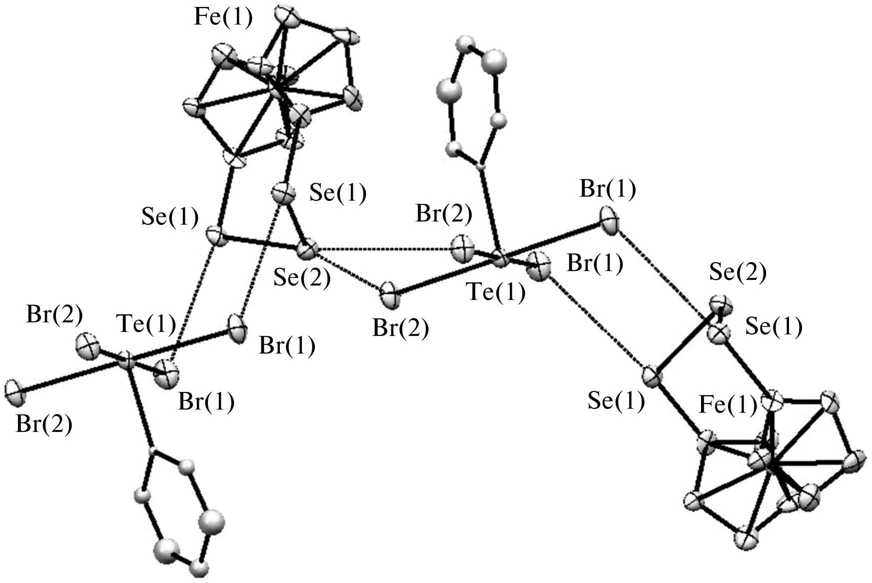


Fig. 2. Molecular structure of compound **III**. Main bond lengths (Se(2)–Se(1) 2.3378(15), Te(1)–Br(1) 2.6670(13), Te(1)–Br(2) 2.7012(13), and Fe(1)–$Cp_{centroid}$ 1.712 Å typical of ferricinium cation) and intermolecular contacts (Br(1)–Se(1) 3.521(2) and Br(2)–Se(2) 3.490(2) Å). Hydrogen atoms are omitted.

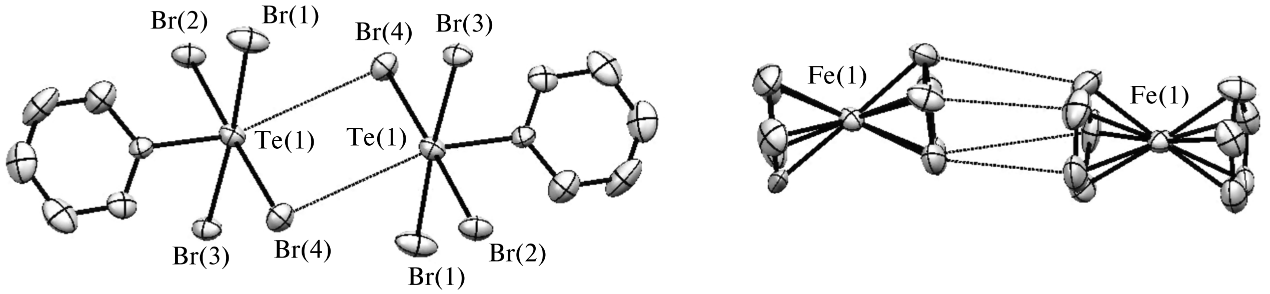
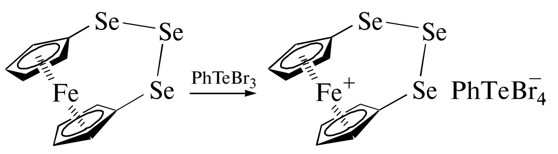


Fig. 3. Molecular structure of $\{[Fc]^+[\ PhTeBr_4]^-\}_2$ (**IVa**). Hydrogen atoms are omitted.

Instead of this, the Se atom, as in the case of diphenyldiselenium, is coordinated to the Br_2 molecule according to the type of a charge-transfer complex to give $[C_8H_{12}Br_2Se]Br_2$ [13].

The predominant oxidation of the iron atom in the ferrocene ring of complex **I** without the decomposition of the latter occurs upon the treatment of compound **I** with phenyltellurium tribromide to form salt **III** containing the same cation but with the $PhTeBr_4^-$ anion (Fig. 2)



It should be mentioned that ferrocene itself undergoes a similar oxidation under the action of $PhTeBr_3$

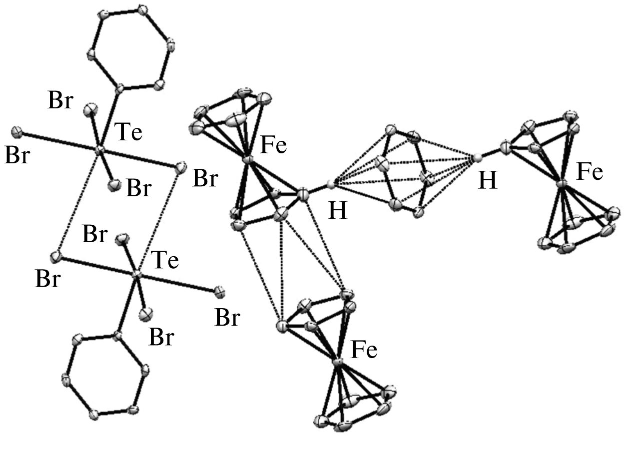


Fig. 4. Molecular structure of $\{[Fc]^+[\ PhTeBr_4]^-\}_2 \cdot C_6H_6$ (**IVb**). Hydrogen atoms that are not involved in the H–π interaction are omitted.

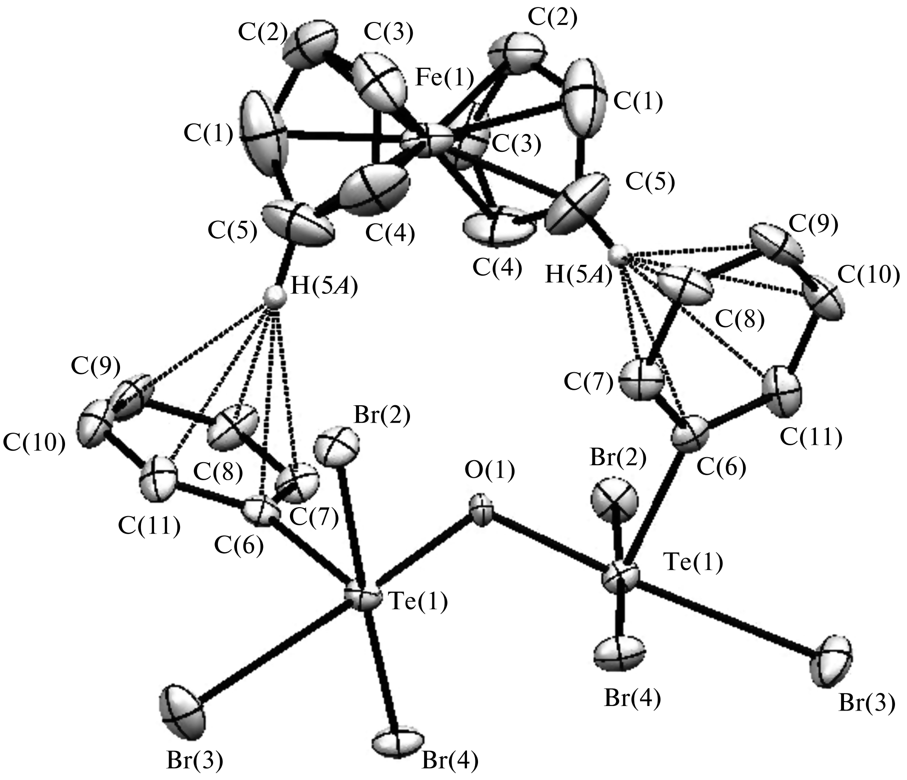
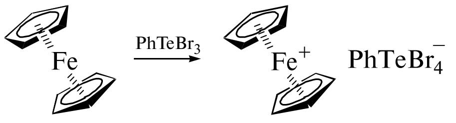


Fig. 5. Molecular structure of etherate $[Fc]^{+}[Ph_2Te_2Br_6OH]^{-} \cdot 0.5(C_2H_5)_2O$ (**V**). Hydrogen atoms that are not involved in the H–π interaction are omitted.



Depending on the crystallization conditions, three different types of interaction between cations and anions were distinguished. In the first case (crystallization from a CH_2Cl_2–THF (1 : 1) mixture), the anions form dimers due to the formation of asymmetrical bromide bridges between the tellurium atoms (intranionic Te–Br bond lengths 2.683–2.733(1) Å, interanionic Te–Br bond lengths 3.803(1) Å, whereas two cations exhibit a stacking interaction between the rings at a distance of 3.427 Å.

For crystallization from a CH_2Cl_2–THF–benzene (1 : 1 : 1/2) system, associates **IVa** having nearly the same Te–Br distances (intranionic 2.6622(8) and 2.7188(8) Å, interanionic 3.6712(6) Å) additionally include a molecule of crystallization benzene weakly interacting with the C–H bonds of the cyclopentadienyl rings (benzene$_{\text{centroid}}$–H(10) 2.664 Å) with retained intercationic stacking interactions between the rings (Cp–Cp$_{\text{centroid}}$ 3.630 Å).

For crystallization from dichloromethane with the addition of nonabsolute (moist) THF and ether, two tellurium atoms of the $PhTeBr_3$ groups are linked through the hydroxyl bridge (Te(1)–O(1) 1.988 Å, Te(1)O(1)Te(1) angle 120.6°) to form an unusual binuclear monoanion $Ph_2Te_2Br_6OH^-$, which includes Te–Br bonds (2.654(1), 2.720(1), and 2.890(1) Å) and is weakly bound by its phenyl groups to the C–H protons of the cyclopentadienyl ligands (Ph$_{\text{centroid}}$ –H(5A) 2.428 Å). Solvate ether molecules are also present in crystal (omitted in Fig. 3).

Thus, the oxidation of ferrocenyl triselenide, as that of ferrocene, by bromine proceeds with the partial decomposition of the ferrocenyl ring and the formation of the $FeBr_4^-$ anion. Under the same conditions, the oxidation of ferrocenyl triselenide and ferrocene by phenyltellurium tribromide does not decompose the ferrocenyl ring and forms the $PhTeBr_4^-$ anion in combination with cations $\{[FcSe_3]^+$ or Fc^+, respectively. In the last case, the formation of solvates with benzene or ether and the partial hydrolysis of the $PhTeBr_4^-$ anion to form the $Ph_2Te_2Br_6OH^-$ anion are possible, depending on the crystallization conditions.

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