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# Halogen and Hydrogen Bonds in Co-Crystalline Ferrocenium Organotellurium Halide Salts

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**Abstract**—The reactions of ferrocene and decamethylferrocene with vinyltellurium trichloride Ph(Cl)C=C(Ph)$TeCl_3$ afford unusual co-crystalline salts $[Cp_2Fe]^+Cl^-$Ph(Cl)C=C(Ph)$TeCl_2OH$ (**I**) and $[(C_5Me_5)_2Fe]^+Cl^-$(Ph(Cl)C=C(Ph)$TeCl_2OH$) (**II**). The Ph(Cl)C=C(Ph)$TeCl_2OH$ molecule in these salts is neutral and forms only non-covalent (hydrogen and chalcogen) bonds with the chloride ion. The hydrolytic replacement of a chlorine atom not involved in the three-center four-electron Cl–Te–Cl bond in Ph(Cl)C=C(Ph)$TeCl_3$ is due to the general moisture sensitivity of organic telluriium halides, and the accompanying oxidation of ferrocene is not a necessary condition for the formation of Ph(Cl)C=C(Ph)$TeCl_2OH$ (**III**). (CCDC nos. 1908530 (**I**), 1908531 (**II**), 1908532 (**III**).)

*Keywords:* halogen bonds, chalcogen bonds, hydrogen bonds, co-crystalline salts, tellurium halides, ferrocene, X-ray diffraction

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## INTRODUCTION

In the last decade, active research into halogen bonds [1], related chalcogen bonds [2], and other so-called σ-hole interactions [3] have induced an explosive growth of the number of studies addressing fundamental and applied aspects of non-covalent intermolecular contacts (called also secondary, or nonvalence contacts). This, in turn, provided new tools for the design of crystals and functional materials [4, 5] and attracted considerable attention and resources to co-crystal engineering [6, 7]. Large diversity, ingenious combinations of components in co-crystals, in particular, their increasing role in modern pharmaceutics brought about the necessity to refine and revise the nomenclature and classification of binary (and more) crystalline systems [8, 9].

In the products of reactions of ferrocene with $PhTeBr_3$ that we described previously, two types of structures were observed: (1) $Cp_2Fe^+[PhTeBr_4]^-$, a compact structure with a clear separation into dimeric $[PhTeBr_3(\mu\text{-}Br)]_2^{2-}$ anions and stacks of $Cp_2Fe^+$ cations formed via π–π stacking interactions between the ferrocenium Cp rings and (2) partially hydrolyzed ferrocenium oxo-phenyltellurium tribromide $[Cp_2Fe^+\text{-}[(PhTeBr_3)_2(\mu\text{-}O)]^-$ in which the $Fe^+$ cations are located between the $[(PhTeBr_3)_2(\mu\text{-}O)]^-$ anions and are bound to them via C–H···Te and C–H···πPh hydrogen bonds (Fig. 1) [10].

In order to pursue these studies and to explore approaches to the targeted design of hybrid co-crystals containing metal complex and organoelement components, we studied the formation and structure of the products of ferrocene co-crystallization with the vinyl trichlorotelluride Ph(Cl)C=C(Ph)$TeCl_3$.

## EXPERIMENTAL

Commercial $(C_5H_5)_2Fe$ and $(C_5Me_5)_2Fe$ were recrystallized prior to use. Ph(Cl)C=C(Ph)$TeCl_3$ was prepared by a reported procedure [11]. Organic solvents were dried by standard procedures.

**Synthesis of $[Cp_2Fe]^+Cl^-$Ph(Cl)C=C(Ph) $TeCl_2$-OH (I).** A yellow-orange solution of ferrocene (9 mg, 0.05 mmol) in $CH_2Cl_2$ (0.1 mL) was placed in a test tube (5 mm inner diameter), and a colorless solution of Ph(Cl)C=C(Ph)$TeCl_3$ (22 mg, 0.05 mmol) in $CH_2Cl_2$ (0.1 mL) was carefully added dropwise. The contact area between the solutions acquired a green color typical of the ferrocenium cation; also, black-green solid particles were formed at the contact between the solutions. The test tube was purged with argon, sealed with several parafilm layers, and left in the dark at room temperature. After 2 days, the solvent evaporated almost completely and uniform green prismatic crystals, suitable for X-ray diffraction, were deposited on the tube wall.

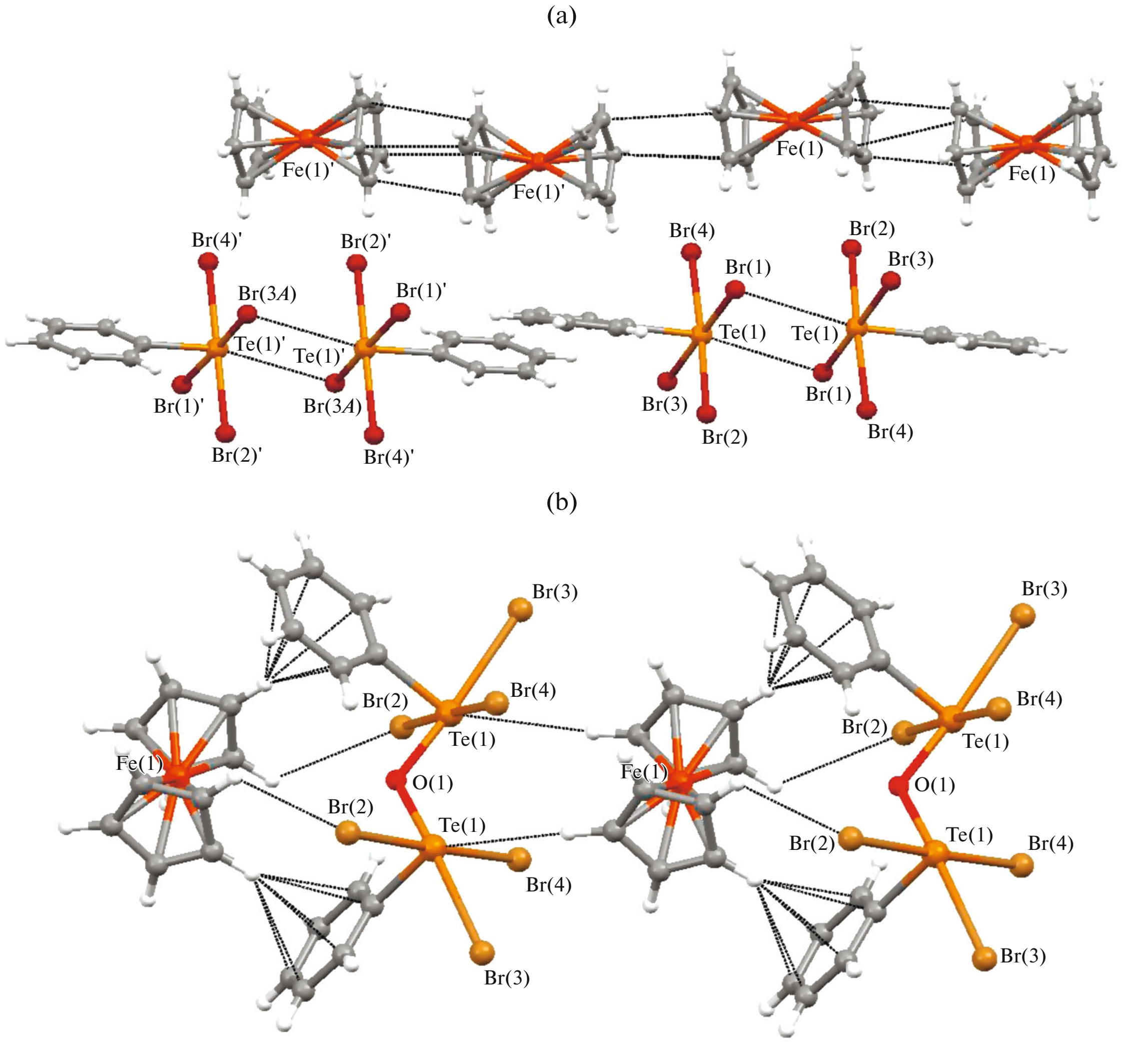


**Fig. 1.** Fragments of chain structure in the crystal packing of (a) $Cp_2Fe^+[PhTeBr_4]^-$ and (b) $[Cp_2Fe]^+[(PhTeBr_3)_2(\mu\text{-}O)]^-$ [10].

**Synthesis of $[(C_5Me_5)_2Fe]^+Cl^-(Ph(Cl)C=C(Ph)TeCl_2OH)$ (II).** A yellow-orange solution of decamethylferrocene (16 mg, 0.05 mmol) in $CH_2Cl_2$ (0.1 mL) was placed in a test tube (5 mm inner diameter), and a colorless solution of Ph(Cl)C=C(Ph)$TeCl_3$ (22 mg, 0.05 mmol) in $CH_2Cl_2$ (0.2 mL) was carefully added dropwise. The contact area between the solutions acquired a green color typical of the ferrocenium cation, but no precipitation or formation of solid particles was observed in the contact area. The test tube was purged with argon, sealed with several parafilm layers, and left in the dark at room temperature. After 5 days, the solvent evaporated almost completely and uniform green prismatic crystals, suitable for X-ray diffraction, were deposited on the tube wall.

**Synthesis of $Ph(Cl)C=C(Ph)TeCl_2OH$ (III).** A solution of Ph(Cl)C=C(Ph)$TeCl_3$ (22 mg, 0.05 mmol) in DMSO (0.1 mL) was placed in a test tube (5 mm inner diameter), plugged with a cotton plug, and left in a light- and dust-protected place at room temperature. After 2 weeks, uniform colorless prismatic crystals, suitable for X-ray diffraction, were formed on the tube bottom under the solvent layer.

**X-ray diffraction** studies were carried out on Bruker APEX II CCD (**II**, **III**) and Agilent Oxford (**I**) diffractometers. Absorption corrections were applied by multiple measurements of equivalent reflections using the SADABS software [12]. The structures of **I**–**III** were solved by the direct method and refined by the least squares method on $F^2$ in the anisotropic approximation for non-hydrogen atoms using the SHELXTL software package [13]. The positions of the H atoms were calculated geometrically. Details of X-ray diffraction experiment and structure refinement for **I**–**III** are summarized in Table 1, and selected distances and bond angles are given in the captions to Figs 2–4.

**Table 1.** Crystal data and structure refinement details for **I–III**

| Parameter | Value | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| Molecular formula | $C_{38}H_{32}O_2Cl_7Fe_1Te_2$ | $C_{48}H_{52}O_2Cl_7FeTe_2$ | $C_{12}H_{16}O_2SCl_3Te$ |
| $M$ | 1080.77 | 1220.93 | 458.26 |
| Radiation (λ, Å) | Cu$K_\alpha$ (1.54184) | Mo$K_\alpha$ (0.71073) | Mo$K_\alpha$ (0.71073) |
| $T$, K | 293 | 150 | 150 |
| System | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ | $Pc$ |
| $Z$ | 4 | 8 | 8 |
| $a$, Å | 17.4427(3) | 30.1203(19) | 12.5710(11) |
| $b$, Å | 15.5567(3) | 9.8261(6) | 12.4019(11) |
| $c$, Å | 14.8766(3) | 21.636(2) | 19.3794(17) |
| α, deg | 90 | 90 | 90 |
| β, deg | 100.7562(18) | 128.9990(10) | 106.986(2) |
| γ, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 3965.85(13) | 4976.5(7) | 2889.5(4) |
| ρ(calcd.), g/cm$^3$ | 1.809 | 1.628 | 2.107 |
| μ, cm$^{-1}$ | 190.35 | 18.65 | 27.52 |
| $F$(000) | 2100 | 2420 | 1784 |
| $2\theta_{max}$, deg | 135 | 50 | 50 |
| Number of measured reflections | 15834 | 29609 | 35020 |
| Number of unique reflections | 7521 | 6634 | 15226 |
| Number of reflections with $I > 2\sigma(I)$ | 5420 | 5691 | 11370 |
| Number of refinement parameters | 459 | 278 | 623 |
| $R_1$ | 0.0497 | 0.0253 | 0.0630 |
| $wR_2$ | 0.1330 | 0.0635 | 0.1784 |
| GOOF | 1.030 | 1.047 | 0.977 |
| Residual electron density (min/max), e Å$^{-3}$ | 1.348/–0.833 | 0.626/–0.369 | 2.603/–1.364 |

Atomic coordinates and other parameters of the structures of **I–III** are deposited with the Cambridge Crystallographic Data Centre (CCDC № 1908530 (**I**), 1908531 (**II**), 1908532 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The replacement of $PhTeBr_3$ by Ph(Cl)C=C(Ph)$TeCl_3$ in the reaction with ferrocene also leads to ferrocene oxidation to the $Cp_2Fe^+$ monocation and partial hydrolysis of Ph(Cl)C=C(Ph)$TeCl_3$ to Ph(Cl)C=C(Ph)$TeCl_2OH$, which forms hydrogen (O–H···Cl ~2.5 Å) and chalcogen (Te···Cl ~3.3 Å) bonds with the chloride anion. The crystal of **I** has one chloride anion and two Ph(Cl)C=C(Ph)$TeCl_2OH$ molecules per ferrocenium cation. Unlike $PhTeBr_3$, which forms the $PhTeBr_4^-$, anion, the fourth position in the tellurium equatorial plane in Ph(Cl)C=C(Ph)$TeCl_3$ is shielded by the vinylic chlorine atom; therefore, the hydroxyl group replaces one of the three chlorine atoms at tellurium. It is noteworthy that this is chlorine not involved in the 3-center 4-electron Cl(2)–Te(1)–Cl(3) bond.

Unlike $[PhTeBr_3(\mu\text{-}Br)]_2^{2-}$ or $[Cp_2Fe]^+[(PhTeBr_3)_2(\mu\text{-}O)]^-$, which are classified as salts (not cocrystals), complex **I** is a non-solvated salt type cocrystal, since its Ph(Cl)C=C(Ph)$TeCl_2OH$ moiety is neutral and forms only non-covalent (hydrogen and chalcogen) bonds with the chloride ion. The environment of the tellurium central atom is a distorted Ψ-octahedron with a 3-center 4-electron Cl–Te–Cl system and two chalcogen bonds: Te···Cl(1) (3.271(2) Å) with the chloride anion and Te···Cl(1*A*)

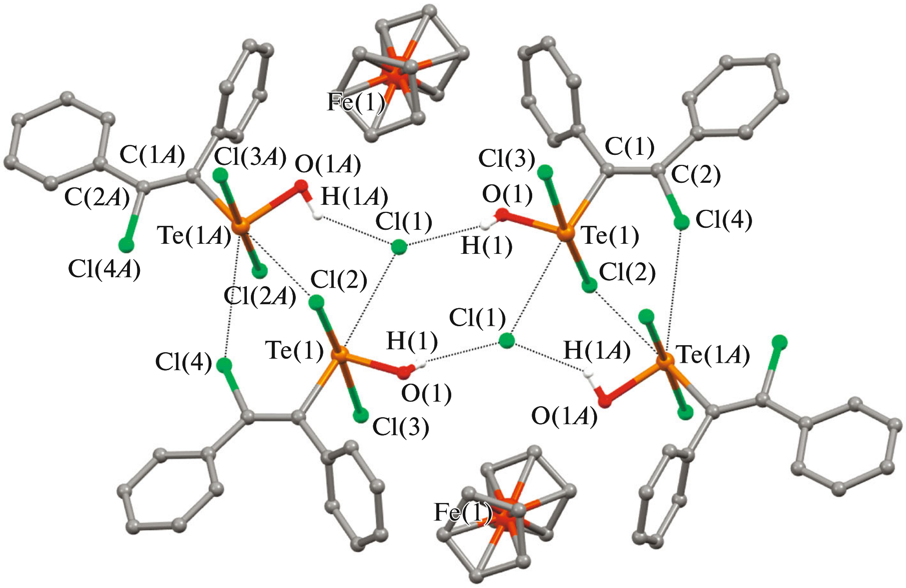


**Fig. 2.** Fragment of the crystal packing of **I**; intramolecular distances: Te(1)–Cl(3), 2.521(2); Te(1)–Cl(2), 2.495(2); Te(1)–O(1), 1.909(4); Te(1*A*)–Cl(3*A*), 2.454(2); Te(1*A*)–Cl(2*A*), 2.533(2); Te(1*A*)–O(1*A*), 1.908(4) Å; intermolecular distances: H(1*A*)–Cl(1), 2.286; H(1)–Cl(1), 2.362; Te(1*A*)–Cl(2), 3.601(2); Te(1)–Cl(1), 3.271(2) Å; intramolecular angles: Cl(3)Te(1)Cl(2), 174.54(6)°; C(1)Te(1)O(1), 94.3(2)°; C(1*A*)Te(1*A*)O(1*A*), 94.2(2)°; intermolecular angles: Cl(3*A*)-Te(1*A*)Cl(2*A*), 174.56(7)°; C(1)Te(1)Cl(1), 166.0(2)°; C(1*A*)Te(1*A*)Cl(2), 173.1(2)°.

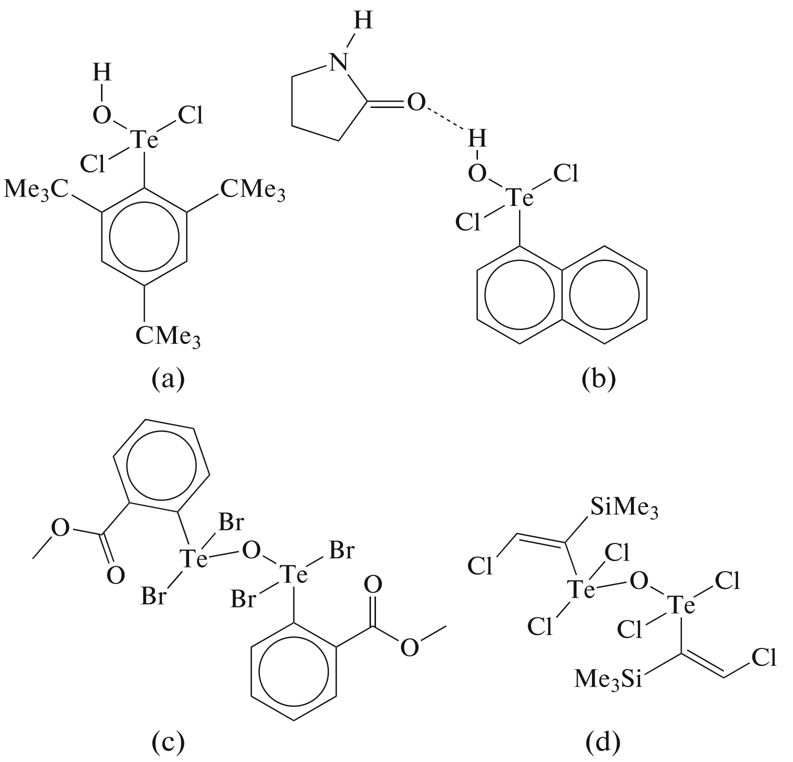
(3.601(2) Å) with the chlorine atom of the Cl–Te–Cl group of the neighboring molecule (Fig. 2).

Co-crystalline salt **II** of the same type is formed with decamethylferrocene under similar conditions. In this case, unlike the case of **I**, no precipitation or formation of solid particles was observed, which may be attributable to better solubility of decamethylferroceneium $(C_5Me_5)_2Fe^+$ salts compared with ferrocenium $(C_5H_5)_2Fe^+$ salts. The crystal of **II** contains one chloride anion per decamethylferrocenium cation and, as in **I**, two Ph(Cl)C=C(Ph)$TeCl_2OH$ molecules, which form O–H···Cl hydrogen bonds (H···Cl ~2.36 Å) and also chalcogen bonds with the chloride anion (Te(1)···Cl(4) ~3.15 Å) and with chlorine of the Cl–Te–Cl group of the neighboring molecule (Te(1)···Cl(1) ~3.65 Å) (Fig. 3).

The formation of the Ph(Cl)C=C(Ph)$TeCl_2OH$ hydroxy derivative for **I** and **II**, despite the use of dry solvents, is an obvious consequence of the known proneness of organotellurium chlorides to hydrolysis [14]. Nevertheless, it was interesting to find out how much the redox conditions are necessary for hydrolysis. For this purpose, solutions of Ph(Cl)C=C(Ph)$TeCl_3$ in $CH_2Cl_2$ and in DMSO were kept in non-tightly closed test tubes in a place protected from light and dust at room temperature. In the test tube containing dichloromethane solution, only the crystals of starting Ph(Cl)C=C(Ph)$TeCl_3$ were detected after 48 h. In the second test tube, hygroscopic DMSO absorbed water vapor from air for 2 weeks; this water caused both hydrolysis of Ph(Cl)C=C(Ph)$TeCl_3$ and precipitation of water-insoluble Ph(Cl)C=C(Ph)Te-$Cl_2OH$ · DMSO solvate (**IIIa**, Fig. 4). Thus, it was shown that the concomitant oxidation of ferrocene is not a necessary condition for the formation of Ph(Cl)C=C(Ph)$TeCl_2OH$, but in the presence of ferrocene, this reaction proceeds much faster.

The geometry of the Ph(Cl)C=C(Ph)$TeCl_2OH$ molecules in solvate **IIIa** slightly differs from that in **I** and **II** only by the rotation angle of the benzene rings relative to the Te–C=C–Cl plane, but the tellurium environments are virtually identical (see captions to Figs. 2–4). This similarity indirectly confirms the assumption that the Ph(Cl)C=C(Ph)$TeCl_2OH$ molecule in **I** and **II** is neutral. In the crystal lattice of **IIIa**, polymeric chains [Ph(Cl)C=C(Ph)$TeCl_2OH$··· DMSO$]_n$ can be clearly distinguished. In the chains, the DMSO solvate molecule acts as the acceptor of intermolecular O–H···O=S hydrogen bond (H···O ~1.88 Å) and chalcogen bond (Te···O=S ~2.93 Å) and thus additionally links two Ph(Cl)C=C(Ph)$TeCl_2OH$ molecules associated via the Te···Cl(2) chalcogen bond (~3.48 Å, Fig. 4).

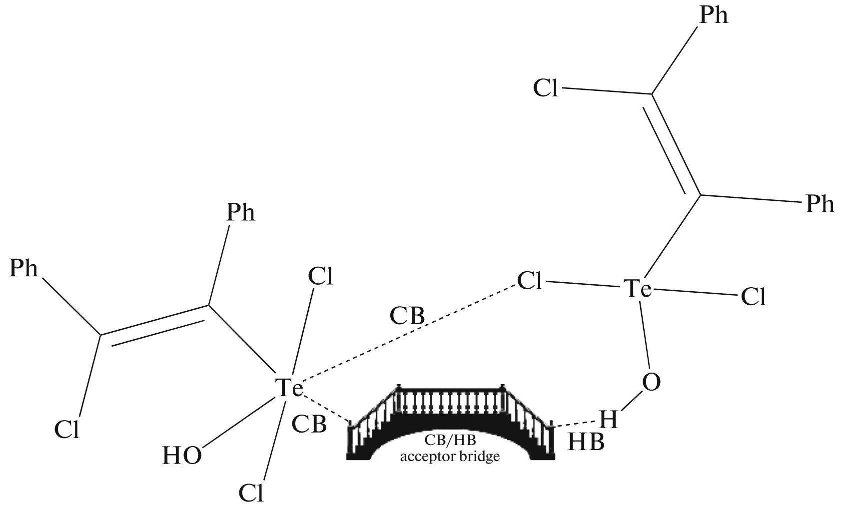
Like in **I**, **II**, and other known structures of organic oxo and hydroxo tellurium halides, oxygen replaces the halogen atom that lies in the equatorial plane relative to the hypervalent X–Te–X group (X = Cl, Br; Scheme 1).


(a) (b)

(c) (d)

**Scheme 1.** Organic oxo and hydroxo tellurium dihalides according to the Cambridge Crystallographic Data Centre [12]): (a) (CIDKIK) dichloro-hydroxy-(2,4,6-tri-*tert*-butylphenyl)telluride(IV) [15], (b) (ECAXEN) dichloro-(1-naphthyl)-hydroxy-telluride(IV) pyrrolidin-2-one [16], (c) (MEGVUR) ($\mu_2$-oxo)-bis(2-methoxycarbonylphenyl)-tetrabromo-ditelluride(IV) [17], (d) (RUFQEP) ($\mu_2$-oxo)-bis((Z)-2-chloro-1-trimethylsilylvinyl)-tetrachloro-ditelluride(IV) [18].

Thus, it was shown that oxidation of ferrocene and its derivatives under the action of 1,2-diphenylvinyltellurium trichlorides is accompanied by partial hydrolysis of Ph(Cl)C=C(Ph)$TeCl_3$ to give co-crystalline $Fc^+Cl^-(Ph(Cl)C=C(Ph)TeCl_2OH)_2$ salts stabilized by a system of hydrogen and chalcogen bonds. The general structural motif of co-crystals of **I**–**IIIa** is shown in Scheme 2.



**Scheme 2.** CB/HB acceptor bridge: $Cl^-$ (**I**, **II**), DMSO (**IIIa**), where CB is the chalcogen bond, HB is hydrogen bond.

The structures of **I**–**IIIa** have a common structural motif: the $(Ph(Cl)C=C(Ph)TeCl_2OH)_2$ dimeric associate formed via the Te···Cl–Te chalcogen bond and additionally stabilized by a chloride bridge (in **I** and **II**)

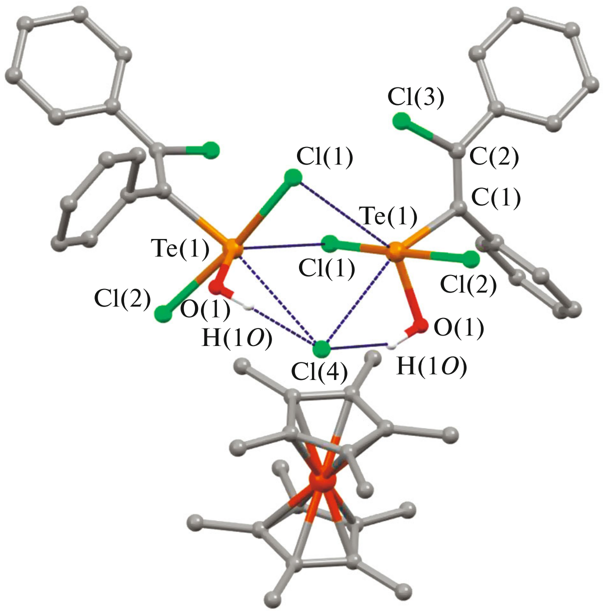


**Fig. 3.** Fragment of the crystal packing of **II**; intramolecular distances: Te(1)–Cl(1), 2.5224(6); Te(1)–Cl(2), 2.4825(6); Te(1)–O(1), 1.926(2) Å; intermolecular distances: H(1O)– Cl(4), 2.3569; Te(1)–Cl(4), 3.1464; Te(1)–Cl(1), 3.654(1) Å; intramolecular angles: Cl(2)Te(1)Cl(1), 173.02(3)°; intermolecular angles: C(1)Te(1)Cl(4), 162.57°; O(1)Te(1)Cl(1), 144.94(6)°.

or a DMSO bridge via a halogen bond (Te···Cl in **I**, **II** or Te···O in **IIIa**) and a hydrogen bond (O–H···Cl in **I**, **II** and O–H···O in **IIIa**) (Scheme 2).

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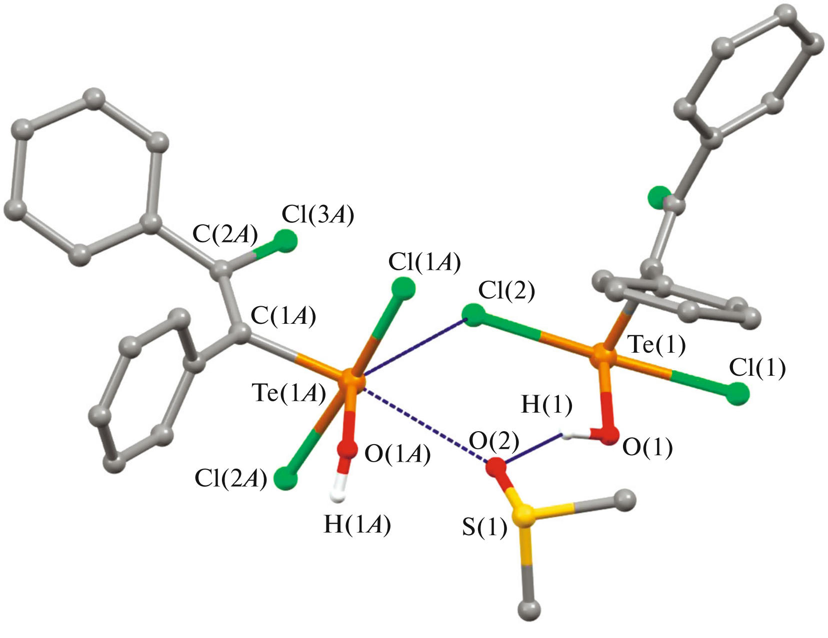

**Fig. 4.** Fragment of the crystal packing of **IIIa**: intramolecular distances: Te(1)–Cl(2), 2.502(4); Te(1)–Cl(1), 2.488(4); Te(1)–O(1), 1.906(9); Te(1*A*)–Cl(1*A*), 2.469(4); Te(1*A*)–Cl(2*A*), 2.516(4) Å; intermolecular distances: H(1)–O(2), 1.88; Te(1*A*)–O(2), 2.93(1); Te(1*A*)–Cl(2), 3.476(4) Å; intramolecular angles: Cl(2)Te(1)Cl(1), 173.1(1)°; Cl(1*A*)Te(1*A*)Cl(2*A*), 173.2(1)°; intermolecular angles: Cl(1*A*)Te(1*A*)O(2), 172.2(4)°; O(1*A*)Te(1*A*)Cl(2), 142.8(3)°.

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## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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