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Bis(4-pyridyl)ditelluride as starting material for the synthesis of zwitterionic compounds and metal complexes

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ABSTRACT

The properties of the derivatives of RTeTeR (R = alkyl, aryl) compounds are highly dependent of the R substituent. To show how versatile are the derivatives of RTeTeR with specific R groups – in this case we use Py* = *p*-(C_5H_4N), we studied the reactions of $Te_2Py^*_2$ with HCl, CH_3I, CH_3I/I_2, $I_2/(Ph_3Te)I$ and $CoCl_2\cdot 6H_2O$, which generate the formation of many classes of compounds: *zwitterions* [(HPy*)$TeCl_2$] (**1**), [(MePy*)TeI_2] (**2**), [(MePy*)TeI_4] (**3**); a telluronium–tellurolate complex (Ph_3Te)[Py*TeI_4] (**4**) and a coordination polymer $\{[Co(Te_2Py^*_2)_2Cl_2]\cdot(Te_2Py^*_2)\}_n$ (**5**). These compounds were characterized by single crystal X-ray diffraction, elemental analysis and infrared spectroscopy.

1. Introduction

RTeTeR compounds have been shown to be suitable starting materials for the synthesis of a variety of tellurium compounds containing the chalcogen in different oxidation states [1–6], including mixed-valence aryltellurenyl compounds [7,8] and related charge-transfer complexes [8–12]. Recently, we could demonstrate that the substituent R (R = phenyl, 2,6-dimethoxyphenyl, mesityl, 2,3,5,6-tetramethylphenyl) has a considerable influence on the stabilization of tellurium halides with different oxidation states [13–18]. Particularly, the influence of the substituent R on the controlled oxidation of the tellurium atom demonstrates that the aryltellurenyl halides can be regarded as key compounds in the synthesis of Te^{I}, Te^{II}, Te^{III} and Te^{IV} products [2,7,9,16,18].

The halogenation reactions of Bbt-substituted ditelluride, BbtTeTeBbt, leading to the formation of the Te^{II}–Te^{IV} mixed-valent tellurenyl fluoride, $BbtTeTe(F)_2Bbt$, and tellurenyl halides, BbtTeX (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl; X = Cl, Br, I) [19]. During the dehalogen-cation reactions of these tellurium halides, it is rational to postulate the formation of a tellurenyl cation species as an intermediate. In this case, it was reported the successful trapping of tellurenyl cation species with butadienes or triphenylphosphane, and the regeneration of the tellurenyl cation species by thermal retro [1 + 4] cycloaddition of the diene adducts.

The crystal structures of organotellurium halide compounds with general formula R_3TeX (R = alkyl, aryl; X = Cl, Br, I) confirm that the compounds are essentially ionic [20–22]. Within the crystals, the packing is determined by Te···X secondary bonds between anion–anion and cation–anion pairs. The primary coordination geometries of the tellurenyl cations are themselves very interesting owing to the occurrence of secondary tellurium–halogen bonds (Te···X), which create exceptional supramolecular structures, leading the formation of polymeric chains, dimeric structures, or monomers with fairly strong intermolecular interactions. The structure and bonding of Ph_3Te^+ cation with relatively large counterions hexachloro-platinate $[PtCl_6]^{2-}$ and -iridate $[IrCl_6]^{2-}$ as well as square planar $[AuCl_4]^-$ and $[PtCl_4]^{2-}$ [22] and also Te^{IV} anionic species $[TeX_6]^{2-}$ and $[PhTeX_4]^-$ [3,4] have shown that the cation–anion interactions are significant in governing the coordination geometry around tellurium and the overall structural features.

In the most cases, the function of the aryl group is limited to the stabilization of the oxidation state of the tellurium atom or to provide an additional donor atom in *ortho*-position for chelate formation [11,23]. With the aim to extend the applicability of the diorganylditellurides we selected the *p*-pyridyl group -Py* = *p*-(C_5H_4N) – for further studies.

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The compound 4,4′-ditellurobispyridine, Py*TeTePy* or $Te_2Py_2^*$, is known since 1993, when von Nagy-Felsobuki and co-workers developed a systematic methodology for the synthesis of telluro- and ditelluro-bispyridines [24]. More recently, Bhasin and co-workers published a one-pot synthetic approach to various pyridyl ditellurides and the X-ray crystal structures of several representatives [25]. The use of synthons containing a pyridyl subunit attached to a chalcogen atom is a very interesting strategy for coordination chemistry owing the different nature of the existent binding sites. In this sense, it is possible to extend our work to the concept of hardness/softness in order to stabilize different interactions with the same synthon. The “soft” chalcogen donor may contribute to the formation of complexes with large Lewis acids and the borderline pyridinic N donor may stabilize the interaction with smaller and harder acceptors [24–30]. Despite of these very interesting characteristics, just a few examples of such compounds are known. This fact can be related with the difficulty to generate such compounds directly from the corresponding halides in good yields [25]. In the last 20 years, we could observe an increasing interest in this kind of ligands, and the most common complexes found in the literature were prepared from the 2-telluro derivatives. It forces the formation of a chelate ring and consequently only saturated complexes have been prepared [26–29]. The advantage of using the 4,4′-derivatives resides in the distance between the two different coordination sites: in this case, the donor atoms are far enough to interact with different centers and it may provide the formation of inner (zwitterions) and outer salts as well as hetero-metallic complexes or coordination polymers. The only example found in the literature related to the latter topic has been published by Ok-Sang and co-workers [30]. The authors describe a reaction of $[Co_2(CO)_8]$ with 3,6-di-*t*-butyl-1.2-benzoquinone, which was carried out in the presence of 4,4′-ditelluridobispyridine and results in a polymer, which was insoluble in organic solvents.

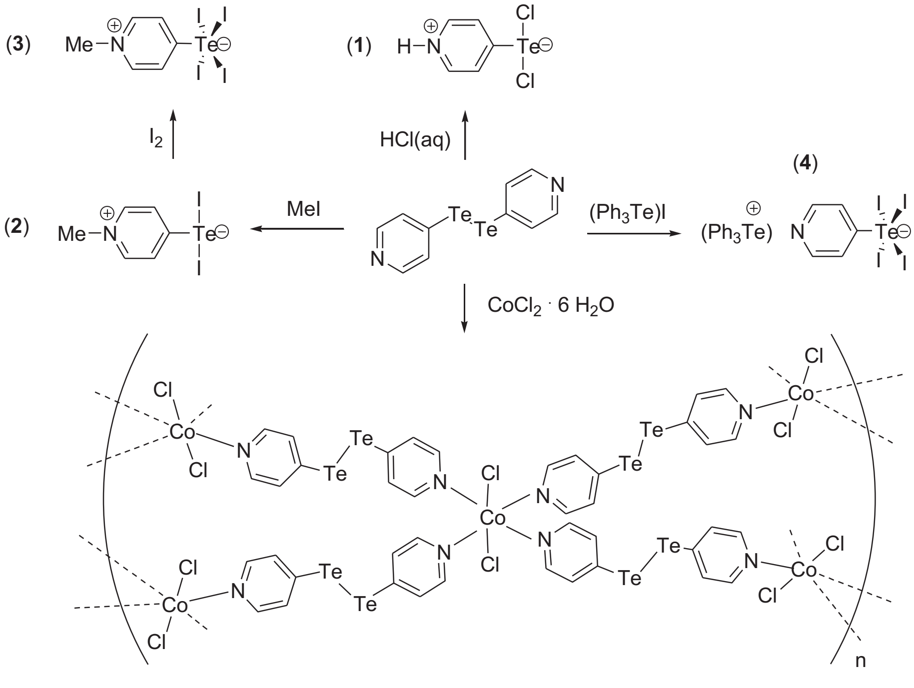
In the course of our ongoing studies to explore the potential of diorganylditellurium compounds as synthons, we present in this article a series of reactions of 4,4′-ditelluridobispyridine, which results in the formation of the zwitterions $[(HPy^*)TeCl_2]$ (**1**), $[(MePy^*)TeI_2]$ (**2**) and $[(MePy^*)TeI_4]$ (**3**); a telluronium–tellurolate complex $(Ph_3Te)[Py^*TeI_4]$ (**4**) and a coordination polymer $\{[Co(Te_2Py_2^*)_2Cl_2]\cdot(Te_2Py_2^*)\}_n$ (**5**). The novel compounds were characterized by single crystal X-ray diffraction, elemental analysis and infrared spectroscopy.

2. Results and discussion

Reactions of 4,4′-ditellurobispyridine with HCl, MeI, a $I_2/(Ph_3Te)I$ stepwise addition or $CoCl_2\cdot 6H_2O$ resulted in the formation of the compounds **1**, **2**, **4** and **5**. Compound **2** is readily oxidized by I_2 to the tellurium(IV) derivative **3**. The reactions described above clearly show the versatility of the diorganylditellurium compounds as synthons. The synthetic routes are presented in Scheme 1. Crystal data and structure refinement information for all compounds are presented in Table 1. Selected bond lengths and angles are summarized in Table 2.

The compounds **1**, **2** and **3** belong to the rare examples of discrete molecular zwitterions containing tellurium. For the compound **1**, the cationic fragment is generated owing to the basicity of the pyridyl group toward the aqueous HCl. Simultaneously, the Te–Te bond of the ditelluride is cleaved and the “T-shaped” tellurolate(II) anion is formed by the coordination of two chloride ions. The formal negative charge of the tellurolate(II) anion is stabilized by the formal positive charge of the pyridinium cation located at the reverse side of the same molecule. The molecular structure of **1** is shown in Fig. 1.

In the molecular structure of the compound **1** the coordination around the tellurium atom is formed by bonding of two chlorines atoms and the carbon atom of the pyridyl substituent. The presence of two stereochemically active lone pairs on a tellurium atom results in a T-shaped coordination geometry. The formal negative charge of the tellurolate(II) anion at one site of the molecule is balanced by the formal positive charge of the pyridinium group at the opposite site of the same molecule. The zwitterionic molecule **1**



(**5**)

Scheme 1. Reactions of $Te_2Py_2^*$.

Table 1
Crystal data and structure refinement for **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_5H_5Cl_2NTe$	$C_{12}H_{14}I_4N_2Te_2$	$C_{30}H_{24}I_8N_2Te_2$	$C_{25}H_{23}I_4N_2O_1Te_2$	$C_{30}H_{24}Cl_2CoN_6Te_6$
Formula weight	277.60	949.05	1456.65	1130.25	1363.98
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1$	Orthorhombic, $Pna2_1$	Orthorhombic, $Pbcm$	Tetragonal, $P4_12_12$
Unit cell dimensions					
a (Å)	11.334(1)	8.088(1)	19.6192(6)	7.9448(7)	9.5086(4)
b (Å)	5.7805(4)	10.919(1)	13.6982(5)	18.718(1)	9.5086(4)
c (Å)	11.895(1)	12.236(2)	10.4206(3)	20.734(2)	41.358(2)
α (°)	90	90	90	90	90.00
β (°)	100.32(1)	92.87(1)	90	90	90.00
γ (°)	90	90	90	90	90.00
Volume (Å^3)	766.7(1)	1079.1(2)	2800.5(2)	3083.3	3739.3(3)
Z; density calculated (g/cm^3)	4; 2.405	2; 2.921	4; 3.455	4; 2.435	4; 2.423
Absorption coefficient (mm^{-1})	4.485	8.419	10.905	5.917	5.221
$F(000)$	512	832	2512	2044	2476
Crystal size (mm)	0.55 × 0.407 × 0.33	0.2 × 0.13 × 0.1	0.14 × 0.086 × 0.061	0.5 × 0.5 × 0.35	0.232 × 0.204 × 0.112
Theta range for data collection θ (°)	2.3–29.2	2.9–29.1	1.8–27	2.7–29.3	1.9–29.6
Index ranges	$-15 \leq h \leq 15$	$-7 \leq h \leq 11$	$-24 \leq h \leq 25$	$-10 \leq h \leq 10$	$-13 \leq h \leq 13$
	$-6 \leq k \leq 7$	$-13 \leq k \leq 14$	$-17 \leq k \leq 17$	$-21 \leq k \leq 25$	$-8 \leq k \leq 13$
	$-16 \leq l \leq 16$	$-16 \leq l \leq 16$	$-13 \leq l \leq 13$	$-28 \leq l \leq 19$	$-53 \leq l \leq 57$
Reflections collected	7721	7157	35,484	11,565	21,326
Independent reflections	2045	4983	5958	4245	5284
Completeness	98.2%	98.5%	99.6%	98.5%	100.0%
Instrument	STOE IPDS	STOE IPDS	Bruker CCD	STOE IPDS	Bruker CCD
Absorption correction	Integration (X-RED 32)	Integration (X-RED 32)	Multi-scan (SADABS)	Integration (X-RED 32)	Multi-scan (SADABS)
Min. and max. transmission	0.1401/0.3612	0.3546/0.7223	0.8417/1.0000	0.1111/0.2246	0.46943/0.76097
Data/restraints/parameters	2045/0/82	4983/1/181	5958/1/218	4245/0/154	5284/0/175
Goodness-of-fit on F^2	1.498	1.051	0.921	1.114	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0263$	$R_1 = 0.0485$	$R_1 = 0.0276$	$R_1 = 0.0560$	$R_1 = 0.0583$
	$wR_2 = 0.0669$	$wR_2 = 0.1196$	$wR_2 = 0.0567$	$wR_2 = 0.1341$	$wR_2 = 0.1695$
R indices (all data)[a]	$R_1 = 0.0323$	$R_1 = 0.0655$	$R_1 = 0.0395$	$R_1 = 0.0729$	$R_1 = 0.0725$
	$wR_2 = 0.0905$	$wR_2 = 0.1236$	$wR_2 = 0.0624$	$wR_2 = 0.1402$	$wR_2 = 0.1810$
Absolute structure parameter		0.1(1)			
Largest diff. peak and hole (e$^-$ Å^{-3})	1.443 and −1.427	2.112 and −1.297	1.298 and −1.209	2.445 and −1.744	5.053 and −2.863

[a] $R_1 = |F_o - F_c|/|F_o|$; $wR_2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.

is *quasi*-planar in the solid, and this feature provides a three-dimensional supramolecular assembly by forming long chains of non-classical N–H···Cl hydrogen bonds and Te···Cl secondary bonds. Fig. 2 illustrates the supramolecular network formed by compound **1**. This arrangement consists of a pair of molecules with antiparallel orientation, which are connected by two Te···Cl interactions (3.763 Å). One chloride from each molecule provides a N–H···Cl interaction (2.531 Å) with a third molecule, generating the supramolecular architecture.

Compound **2** is obtained in moderate yields from a nucleophilic attack of the pyridyl nitrogen atom to the electron deficient carbon atom of MeI, forming a pyridinium cation. The cleavage of the Te–Te bond of 4,4′-ditellurobispyridine and the coordination of two iodine atoms to the tellurium(II) atom generate a T-shaped coordination geometry around the tellurium atom. Similarly to compound **1**, a tellurolate(II) anion is formed at this site of the molecule. In this case the formal negative charge is balanced with the formal charge of the methylpyridinium group. Thus, compound **2** also represents a zwitterionic molecule. The asymmetric unit of **2** consists of a dimeric arrangement (Fig. 3), in which the molecules are connected by two simultaneous Te···I secondary bondings (3.790 Å, 3.829 Å). No further important intermolecular interactions are observed for this compound. The reaction of $Te_2Py_2^*$ with MeI also gives a yellow solid, insoluble in organic solvents (except DMSO). The mass spectra for this compound points to a structure built up by a $(Py^*TeMe_2)^+$ or $[(MePy^*)TeMe]^+$ fragment (both forms fit to a $m/z = 237.9863$). As its solution in DMSO quickly decomposes, no further studies were carried out.

Compound **3** was prepared by the oxidation of compound **2** by iodine. The molecular structure of the product, which is also a zwitterion, is shown in Fig. 4. In compound **3**, the tellurium is surrounded by four iodine atoms in the same plane. The carbon atom of the methylpyridinium group and a stereochemically active lone pair gives rise to a square-pyramidal geometry if we take into account only the bonded atoms. In the solid state structure, the asymmetric unit of this compound is formed by two independent molecules of **3** without further important intermolecular interactions.

Compound $Te_2Py_2^*$ and diiodine react to produce Py^*TeI_3 *in situ*, which is converted to the anionic complex after the addition of $(Ph_3Te)I$. An ellipsoid representation of the mixed telluronium/tellurolate adduct **4** is shown in Fig. 5. The $[Py^*TeI_4]^-$ anion shows a distorted octahedral environment around the Te^{IV} atom, with Te···N contacts *trans* to the pyridyl group attached to tellurium. The supramolecular network formed by compound **4** is depicted in Fig. 6. Its structural features are quite different from those found for its analogs in the literature [3,4]. While $(R_3Te)[RTeX_4]$ compounds exhibit typical secondary Te···X interanionic interactions, compound **4** shows a linear anionic chain formed by extremely rare intermolecular Te···$N_{(pyridine)}$ secondary bonds between the anions along the crystallographic a axis (Fig. 6).

Single crystals of $\{[Co(Te_2Py_2^*)_2Cl_2]\cdot(Te_2Py_2^*)\}_n$ (**5**) are formed when a methanolic solution of $Te_2Py_2^*$ is carefully added to an aqueous solution of $CoCl_2\cdot6H_2O$.The crystal structure of **5** consists of a coordination polymer of $[Co(Te_2Py_2^*)_2Cl_2]_n$ and independent molecules of $Te_2Py_2^*$ (Fig. 7). The cobalt atom is surrounded by four pyridyl groups coordinating in equatorial positions and two chlorido ligands in apical positions providing a distorted octahedral geometry around the metal center. This polymeric, three-dimensional structure is formed since the Te–Te bonds remain

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**5**.

Compound		Å		°
1	Te(1)–Cl(1)	2.5205(7)	Cl(1)–Te(1)–Cl(2)	177.04(2)
	Te(1)–Cl(2)	2.6224(7)	C(11)–Te(1)–Cl(1)	91.74(7)
	Te(1)–C(11)	2.120(2)	C(11)–Te(1)–Cl(2)	90.95(7)
	N(1)–H(1)	0.8600		
2	Te(1)–I(1)	2.9942(15)	I(2)–Te(1)–I(1)	174.67(5)
	Te(1)–I(2)	2.9049(15)	I(3)–Te(2)–I(4)	176.08(5)
	Te(2)–I(3)	2.9450(14)	C(11)–Te(1)–I(1)	91.9(4)
	Te(2)–I(4)	2.9509(14)	C(11)–Te(1)–I(2)	91.8(4)
	C(11)–Te(1)	2.143(13)	C(21)–Te(2)–I(3)	92.2(4)
	C(21)–Te(2)	2.155(16)	C(21)–Te(2)–I(4)	91.7(4)
3	I(11)–Te(1)	2.9079(9)	I(12)–Te(1)–I(11)	89.29(2)
	I(12)–Te(1)	2.9065(9)	I(11)–Te(1)–I(14)	89.41(3)
	I(13)–Te(1)	2.9352(9)	I(12)–Te(1)–I(13)	88.25(3)
	I(14)–Te(1)	2.9229(9)	I(14)–Te(1)–I(13)	92.89(3)
	I(21)–Te(2)	2.9312(9)	C(1)–Te(1)–I(11)	89.7(2)
	I(22)–Te(2)	2.9307(8)	I(22)–Te(2)–I(21)	90.97(2)
	I(23)–Te(2)	2.9224(9)	I(24)–Te(2)–I(21)	89.92(3)
	I(24)–Te(2)	2.8973(8)	I(24)–Te(2)–I(23)	90.89(3)
	Te(1)–C(1)	2.168(9)	C(11)–Te(2)–I(22)	88.9(2)
	Te(2)–C(11)	2.166(9)		
4	I(1)–Te(1)	2.9206(7)	I(2)–Te(1)–I(1)	89.95(2)
	I(2)–Te(1)	2.9114(6)	I(1)–Te(1)–I(1)^{i}	179.62(4)
	C(11)–Te(2)	2.097(4)	I(2)–Te(1)–I(1)^{i}	90.06(2)
	C(21)–Te(2)	2.132(13)	I(2)^{i}–Te(1)–I(2)	177.77(4)
			C(1)–Te(1)–I(1)	89.809(18)
			C(1)–Te(1)–I(2)	91.114(18)
5	N(1)–Co(1)	2.319(5)	N(2)^{iii}–Co(1)–N(2)^{iv}	95.7(7)
	C(3)–Te(1)	2.169(5)	N(2)^{iii}–Co(1)–N(1)	90.3(4)
	Cl(1)–Co(1)	2.518(2)	N(2)^{iv}–Co(1)–N(1)	174.0(4)
	N(2)–Co(1)^{ii}	2.298(5)	N(1)–Co(1)–N(1)^{v}	83.6(3)
	Co(1)–N(2)^{iii}	2.298(13)	N(2)^{iv}–Co(1)–Cl(1)	88.4(2)
	Co(1)–N(2)^{iv}	2.298(15)	N(1)–Co(1)–Cl(1)	91.37(18)
	Te(3)–Te(3)^{vi}	2.699(2)	N(1)–Co(1)–Cl(1)^{v}	92.61(18)
	Te(1)–Te(2)	2.6982(10)	Cl(1)–Co(1)–Cl(1)^{v}	174.66(18)
	C(8)–Te(2)	2.118(7)		
	C(11)–Te(3)	2.132(16)		

Symmetry transformations used to generate equivalent atoms: $^{i} = x,-y + 3/2,-z$; $^{ii} = x - 1/2,-y + 3/2,-z + 3/4$; $^{iii} = x + 1/2,-y + 3/2,-z + 3/4$; $^{iv} = y - 1/2,-x + 1/2,z - 1/4$; $^{v} = -y + 1,-x + 1,-z + 1/2$; $^{iv} = -y + 2,-x + 2,-z + 1/2$.

intact. Thus, each 4,4′-ditellurobispyridine molecule acts as bridging ligand between two cobalt atoms. Compound $Te_2Py_2^*$ was also used in reactions with a series of metal chlorides such as $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$. In all cases, we observe immediate precipitation of extremely insoluble compounds.

3. Conclusions

Five novel tellurium compounds, belonging to different chemical classes such as zwitterions, telluronium–tellurolate complexes and coordination polymers, have been prepared by simple reactions starting from 4,4′-ditellurobispyridine. The manifold of the products demonstrates how versatile the use of the pyridyl or others substituent at the diorganylditelluride may be in the synthesis of novel tellurium compounds, particularly in the design of supramolecular aggregates. By choosing other substituents at the R groups of RTeTeR compounds will allow the generation of many others similar classes of compounds, in which strong covalent bonds act together with weak hydrogen bonds, long-range Te···I bonds and coordinate forces in the assembly of supramolecular networks.

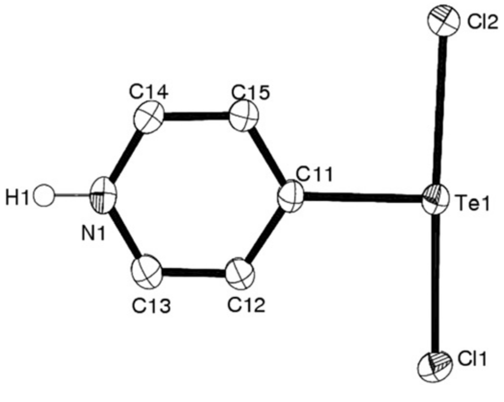


Fig. 1. Asymmetric unit of compound **1**, showing the *quasi*-planar zwitterionic molecule.

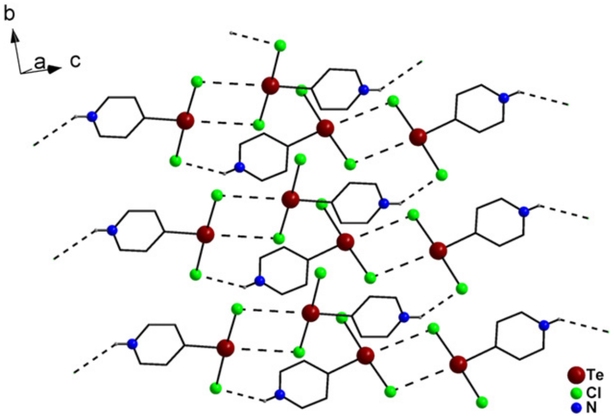


Fig. 2. The supramolecular arrangement of compound **1**. Hydrogen atoms were omitted for clarity, except those related to N–H···Cl interactions.

After this initial article, we have already started to modify the properties associated with the ditellurides RTeTeR and their derivatives, e.g. their solubility in water.

4. Experimental section

4.1. General

Solvents and standard reagents were obtained commercially (Aldrich or Sigma) and used without further purification, $(Ph_3Te)I$ and $Te_2Py_2^*$ were prepared following literature procedures [5,24,31]. Elemental analyses (CHN) were obtained with a VARIO EL analyzer (Elementar Analysensysteme GmbH) from São Paulo University, Brazil. Infrared spectra were measured using a Bruker Tensor 27 mid-IR spectrometer.

4.2. X-ray structure determinations

Bruker CCD X8 Kappa APEX II or STOE IPDS 2T diffractometers operated using graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$ Å) were used for the X-ray structure analyses. The

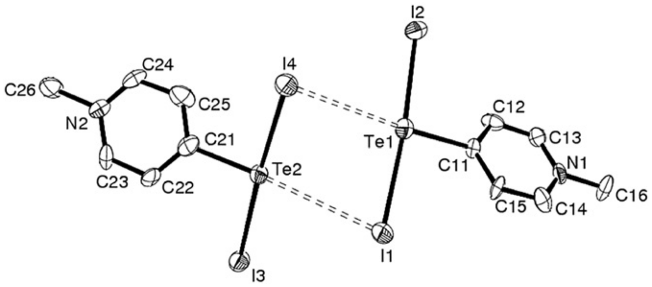


Fig. 3. Asymmetric unit of compound **2**, showing the pseudo-dimeric arrangement promoted by secondary Te···I bonds.

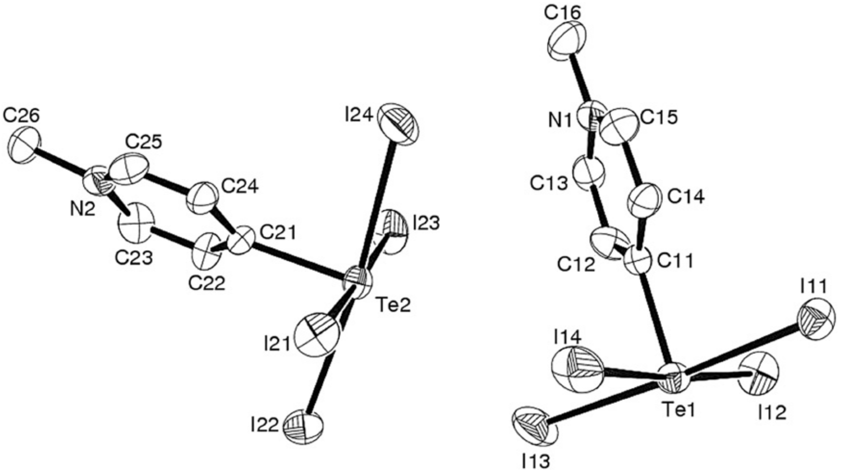


Fig. 4. Asymmetric unit for compound **3**, in this case there are no secondary Te···I interactions.

structures were solved by direct methods with SHELXS and refined with SHELXL with anisotropic displacement parameters for all non-hydrogen atoms [32]. The positions of hydrogen atoms bonded to carbon atoms were calculated for idealized positions and treated with the "riding model" option of SHELXL. The positions of hydrogen atoms bonded to nitrogen atoms were located in the final Fourier maps and refined with isotropic displacement parameters. More information about the structure determinations is given in Table 1.

4.3. Synthesis of [(HPy*)TeCl$_2$] (**1**)

To a solution of $Te_2Py_2^*$ (0.412 g; 1 mmol) in 5 mL of CH_2Cl_2, 5 mL of aqueous HCl (37%) were added. The system was closed and the mixture was kept under stirring for 3 h. The yellow solid material formed was collected by filtration and re-crystallized from MeOH. Yield: 0.260 g, 45% based on $Te_2Py_2^*$ taken.

Properties: yellow crystalline substance. $C_6H_7NTeCl_2$ (277.61 g/mol). C, H, N-Analysis (%), found: C = 21.71, H = 1.83, N = 5.02; calc.: C = 21.63, H = 1.83, N = 5.05. IR (cm^{-1}, KBr): 3217, 3133 [ν(N–H)]; 3049, 2916 [ν(C_{aryl}–H)]; 1615, 1580, 1470 [ν(C–C), ν(C–N)]; 1262, 1233, 1204, 1104, 1053 [β(C–H)]; 804 [γ(C–H)]; 762 [β-ring]; 453 [ν(C–Te)].

4.4. Synthesis of [(MePy*)TeI$_2$] (**2**)

To a solution of $Te_2Py_2^*$ (0.412 g; 1 mmol) in 5 mL of CH_2Cl_2, 5 mL of MeI were added. The system was closed and the mixture was kept under stirring for 24 h. The yellow precipitate formed was washed with MeCN and removed by filtration. The resulting dark red solution was evaporated at room temperature to give single crystals of **2**. Yield: 0.150 g, 32% based on $Te_2Py_2^*$ taken.

Properties: dark red crystalline substance. $C_6H_7NTeI_2$ (474.54 g/mol). C, H, N-Analysis (%), found: C = 15.39, H = 1.47, N = 3.02; calc.: C = 15.19, H = 1.49, N = 2.95. IR (cm^{-1}, KBr): 3094, 3048, 2964 [ν(C_{aryl}–H)]; 1615, 1547, 1482, 1445 [ν(C–C), ν(C–N)]; 1324, 1262, 1196, 1095, 1050 [β(C–H)]; 960, 807 [γ(C–H)]; 693 [β-ring]; 471 [ν(C–Te)].

4.5. Synthesis of [(MePy*)TeI$_4$] (**3**)

To a suspension of finely ground (MePy*)TeI$_2$ (0.475 g; 1 mmol) in 10 mL of MeOH, solid I_2 (0.254 g; 1 mmol) was added at r.t. After stirring for 2 h, the black solid formed was collected by filtration and re-crystallized from MeCN. Yield: 0.360 g, 50% based on $Te_2Py_2^*$ taken.

Properties: dark red crystalline substance. $C_6H_7NTeI_4$ (728.35 g/mol). C, H, N-Analysis (%), found: C = 11.38, H = 1.02, N = 2.16; calc.: C = 9.84, H = 0.96, N = 1.92. IR (cm^{-1}, KBr): 3094, 3048, 2924 [ν(C_{aryl}–H)]; 2360 (overtones); 1607, 1557, 1479, 1429 [ν(C–C), ν(C–N)]; 1306; 1268, 1188, 1042 [β(C–H)]; 805[γ(C–H)]; 695[β-ring]; 486 [ν(C–Te)].

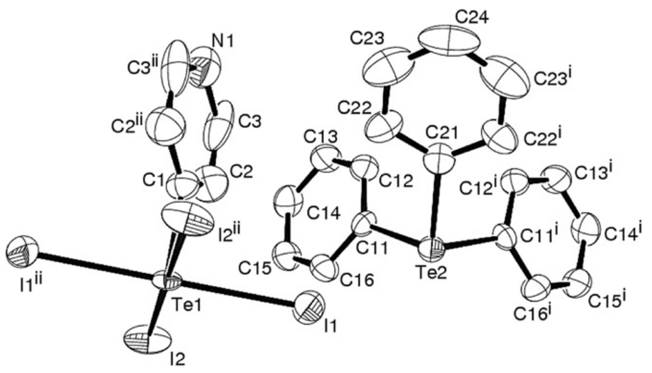


Fig. 5. Asymmetric unit of compound **3**. Hydrogen atoms were omitted for clarity. Symmetry operations to generate equivalent atoms: ^{i} = $x,y,-z+1/2$; ^{ii} = $x,-y+3/2,-z+1$.

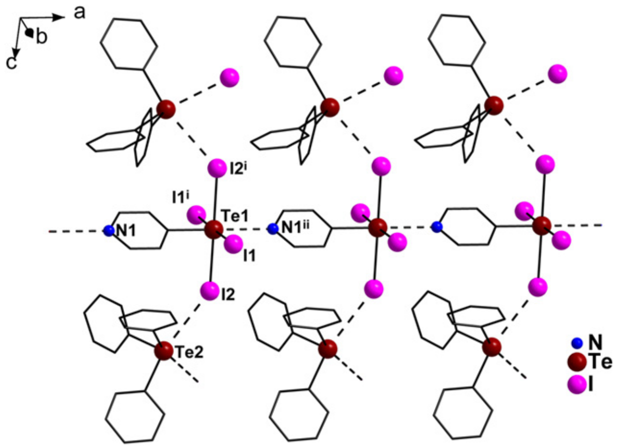


Fig. 6. The supramolecular arrangement of compound **4**, with emphasis on the linear connection between the anions via Te···N interactions. Hydrogen atoms were omitted for clarity. Symmetry operations to generate equivalent atoms: ^{i} = $x,-y+3/2,-z+1$. ^{ii} = $1+x,y,z$.

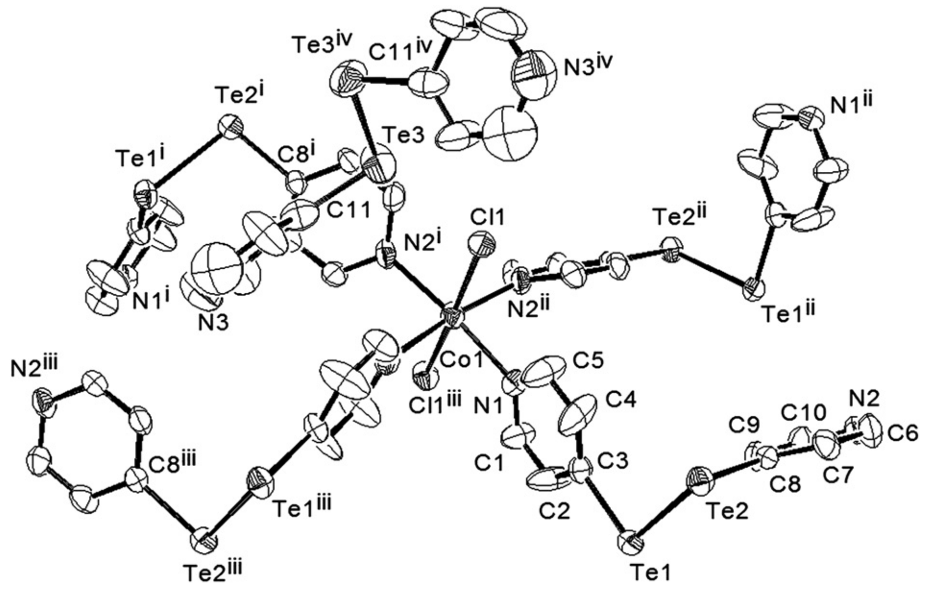


Fig. 7. A view of the polymeric structure of compound **5** showing the distorted octahedral coordination around the cobalt atoms. Hydrogen atoms were omitted for clarity. Symmetry operations to generate equivalent atoms: $^{i} = -x + 1/2, y - 1/2, -z + 7/4$; $^{ii} = -y + 1, -x + 1, -z + 3/2$; $^{iii} = -x + 1/2, y + 1/2, -z + 7/4$.

4.6. *Synthesis of (Ph$_3$Te)[Py*TeI$_4$] (**4**)*

A solution of Te$_2$Py$_2^*$ (0.412 g; 1 mmol) in 30 mL of MeOH was cooled in an ice bath, and solid I$_2$ (0.761 g; 3 mmol) was added. After stirring for 1 h, the ice bath was removed and the system was kept at r.t. for 30 min. Then, solid (Ph$_3$Te)I (0.972 g; 2 mmol) was added to the dark mixture. After 1 h under stirring, the dark solid was collected by filtration and re-crystallized from MeCN. Yield: 1.743 g, 80% based on Te$_2$Py$_2^*$ taken.

Properties: dark red crystalline substance. C$_{23}$H$_{19}$NTe$_2$I$_4$ (1072.22 g/mol). C, H, N-Analysis, found: C = 25.54, H = 1.74, N = 1.52%; calc.: C = 25.76, H = 1.79, N = 1.31%. IR (cm^{-1}, KBr): 3045 [ν(C$_{aryl}$–H)]; 1611, 1572, 1557, 1475 [ν(C–C), ν(C–N)]; 1397; 1262, 1114, 1052 [β(C–H)]; 995, 795 [γ(C–H)]; 737, 685 [β-ring]; 462 [ν(C–Te)].

4.7. *Synthesis of $\{[Co(Te_2Py_2^*)_2Cl_2]\cdot(Te_2Py_2^*)\}_n$ (**5**)*

To a diluted solution of CoCl$_2$·6H$_2$O (0.059 g; 0.25 mmol) in 10 mL of water, a solution of Te$_2$Py$_2^*$ (0.204 g; 0.5 mmol) in 15 mL of methanol was slowly added dropwise. After the diffusion of the solutions, single crystals of compound **5** were isolated as a dark red microcrystalline material. Yield: 0.149 g, 60% based on Te$_2$Py$_2^*$ taken.

Properties: dark red crystalline substance. C$_{30}$H$_{24}$Cl$_2$CoN$_6$Te$_6$ (1363.99 g/mol). C, H, N-Analysis (%), found: C = 26.95, H = 1.71, N = 6.21; calc.: C = 26.42, H = 1.77, N = 6.16. IR (cm^{-1}, KBr): 3040 [ν(C$_{aryl}$–H)]; 1579, 1534, 1476, 1406 [ν(C–C), ν(C–N)]; 1314; 1213, 1085, 1055, 1009 [β(C–H)]; 811, 792 [γ(C–H)]; 667, 650 [β-ring]; 483, 465 [ν(C–Te)].

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Appendix A. Supplementary material

CCDC 853335–853339 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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