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The Crystal Structure of Bis(triphenylphosphine)iminium Halocyano-4-nitrobenzyltellurates(II), [PNP][4-NO_2-$PhCH_2Te(CN)X$], X = Cl, Br and I

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The structures of $[(Ph_3P)_2N][4\text{-}NO_2\text{-}PhCH_2Te(CN)X]$, I: X = Cl, II: X = Br, III: X = I, have been determined by X-ray methods using diffractometer data collected at room temperature. Full-matrix least-squares refinements led to final conventional *R*-values of 0.048 (3589) for I, 0.051 (3166) for II and 0.036 (5256) for III. (The number of observed reflections in parentheses.)

The compounds crystallize in the triclinic system with the following unit cell dimensions: I: a = 9.833(2) Å, b = 14.435(2) Å, c = 16.307(2) Å, α = 66.09(2)°, β = 78.63(2)°, γ = 71.77(2)°; II: a = 9.902(2) Å, b = 14.464(2) Å, c = 16.392(1) Å, α = 65.95(1)°, β = 78.57(1)°, γ = 71.97(1)°, III: a = 12.578(2) Å, b = 12.730(3) Å, c = 14.258(2) Å, α = 77.68(2)°, β = 79.05(2)°, γ = 69.92(2)°. All three compounds have space group $P\bar{1}$(No. 2), Z = 2; I and II are isomorphous.

Tellurium and the arrangement of the atoms bonded to tellurium are T-shaped and of the three-center-two-electron type. The halogen atoms are linked to the tellurium atom approximately *trans* to the cyano group with fairly short Te–X bond distances; Te–Cl is 2.923(2) Å in I, Te–Br is 3.100(1) Å in II and Te–I is 3.299(0) Å in III. A comparison with the sum of the van der Waals' radii and with the sum of the covalent distances of the atoms indicates the bond order of the Te–X bonds to be Te–Cl > Te–Br > Te–I. This bond order sequence suggests that symbiosis may play an important role with regard to bond lengths in Te(II)-complexes. In I and II there are weak intermolecular bonds to neighbouring oxygen atoms of 3.449(3) Å (I) and 3.435(5) Å (II). In III the tellurium atom is strictly three-coordinated.

The Te–C(CN) bond lengths are significantly longer, ~0.08 Å, than in the parent organic tellurocyanate while the other bond lengths, bond angles and torsion angles remain essentially the same.

The [PNP]-cations have the non-linear form with a P–N–P bond angle of 137.1(4)° in I, 136.8(4)° in II and 142.8(2)° in III.

Alkyl thiocyanates, RSCN, and alkyl selenocyanates, RSeCN, are readily prepared from the corresponding halides and alkali metal thiocyanates and selenocyanates by the Finkelstein reaction, eqn. (1). The limited solubility of the alkali metal

$$RX + KSCN(KSeCN) \rightarrow RSCN(RSeCN) + KX \quad (1)$$

halides in the usual dipolar organic solvents, protic and aprotic ones, allows the products to be isolated in high yield.[1]

The preparation of organic tellurocyanates, RTeCN, is more difficult since alkali metal tellurocyanates cannot be prepared.[2] Cava and coworkers,[3] however, have recently shown that by employing alkali metal tellurocyanates in dimethyl sulfoxide, made *in situ*, organic tellurocyanates may be formed as depicted by eqn. (1). So far, only substituted benzyl tellurocyanates have been prepared by this method.[3–6]

When using stable onium tellurocyanates[2,7,8] when attempting to prepare organic tellurocyanates according to eqn. (1) in dipolar aprotic solvents in which the tellurocyanate ion is stable,[2] the product is not the expected one but a salt.[9] The anion of this salt was proposed to be the addition compound between the first formed organic tellurocyanate and the displaced halide ion, an alkylcyanohalotellurate(II) anion,[9] eqn. (2). Apparently, an equilibrium between this anion and the organic tellurocyanate exists, eqn. (3).

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$$RX + O^+NCTe^- \rightarrow O^+[RTe(CN)X]^- \quad (2)$$

$$[RTe(CN)X]^- \rightleftarrows RTeCN + X^- \quad (3)$$

In the presence of alkali metal cations this equilibrium is completely shifted to the right due to the limited solubility of the alkali metal halides in dipolar aprotic solvents which is the key to Cava's preparation[3] according to eqn. (1). When using tetraphenylarsonium tellurocyanate, $Ph_4AsTeCN$, the yield of the complex anion, eqn. (2), is moderate.[9] This is due to the fairly limited solubility of the Ph_4As^+-halides and of Ph_4As^+-tellurocyanate as compared with the extreme solubility of the Ph_4As^+-salts of the complex tellurate anions in the usual dipolar aprotic solvents. By addition of diethyl ether to the reaction mixture, the equilibrium, as depicted by eqn. (3), is readily displaced to the right and a mixture of Ph_4As^+-salts is obtained.[9]

However, when using the bis(triphenylphosphine)iminium ion, $[PNP]^+$, as cation, the difference in the solubility of the [PNP]-halides and of the [PNP]-tellurates is greatly diminished allowing the latter salts to be isolated in almost quantitative yield. In the present study we want to report the crystal structures of three such salts:

$[PNP][4\text{-}NO_2\text{-}PhCH_2Te(CN)X]$
$([PNP]^+ = [(Ph_3P)_2N]^+)$

I:X=Cl II:X=Br III:X=I

The 4-nitrobenzyl group was chosen since the structure of the parent organic tellurocyanate, $4\text{-}NO_2\text{-}PhCH_2TeCN$, has recently been described[6] allowing a direct comparison. Furthermore, the high stability of this tellurocyanate allowed an alternative and facile synthesis of the adducts in acetone or acetonitrile according to eqn. (4) as a proof of their composition.

$$4\text{-}NO_2\text{-}PhCH_2TeCN + [PNP]X \rightarrow [PNP][4\text{-}NO_2\text{-}PhCH_2Te(CN)X] \quad (4)$$

EXPERIMENTAL

Solvents. All solvents used were purified and dried according to standard procedures and distilled in an argon atmosphere prior to use.

Materials. The preparation and purification of [PNP]X (X=Cl^-, Br^-, I^- and $TeCN^-$) has been described.[1] The 4-nitrobenzyl halides were crystallized from cyclohexane prior to use and stored dark in the cold. The corresponding tellurocyanate was prepared as reported[6] and crystallized from dichloromethane prior to use. All operations involving [PNP]TeCN and the [PNP]-tellurates in solution were carefully performed in argon-flushed solvents. In the solid state, however, these compounds are stable for months without any precautions with regard to moisture, oxygen or light.

I. *Bis(triphenylphosphine)iminium chlorocyano-4-nitrobenzyltellurate(II)*, $[PNP][4\text{-}NO_2\text{-}PhCH_2Te(CN)Cl]$. To 0.5 g (0.003 M) 4-nitrobenzyl chloride in 40 ml acetone was added 1.73 g (0.0025 M) [PNP]-tellurocyanate dissolved in 20 ml acetone. The mixture was stirred for 24 h at room temperature in a closed bottle. Traces of Te and TeO_2 was removed by filtration whereupon nearly all the solvent was removed *in vacuum*. A fairly large amount of diethyl ether was added until turbidity and the first crop of precipitate, essentially [PNP]Cl, was discarded. After two days at ~ -20 °C the yellowish product was isolated in close to quantitative yield. This purification procedure was repeated once and 1.60 g, 76 %, was finally obtained. This compound could be prepared in about the same yield from 4-nitrobenzyl tellurocyanate and [PNP]Cl in acetone or acetonitrile according to eqn. (4). M.p. ~120 °C (dec.). (Found: C 61.61; H 4.34; N 4.95. Calc. for $C_{44}H_{36}ClN_3O_2P_2Te$: C 61.18; H 4.20; N 4.86). IR(KBr): The spectrum (400–4000 cm^{-1}) was as the sum of the spectra of [PNP]Cl and the parent organic tellurocyanate except that no peak due to C≡N stretch in the 2000–2200 cm^{-1} region could be detected. UV(8×10^{-4} M in MeCN, 1 cm path length): A shoulder to the NO_2-peak at ~355 nm, shifted some 15 nm toward higher wave length as compared with 4-nitrobenzyl tellurocyanate[6] but with essentially unaltered extinction coefficient, log ε~3.3. NMR (MeCN): 4.36(s,2H), as in the organic tellurocyanate.[6]

II. $[PNP][4\text{-}NO_2\text{-}PhCH_2Te(CN)Br]$. From 0.24 g (0.0011 M) $4\text{-}NO_2\text{-}PhCH_2Br$ and 0.69 g (0.001 M) [PNP]TeCN a yield of 0.75 g. 83 %, was obtained according to the procedure described for the corresponding chloro compound, I. This compound could also be prepared from [PNP]Br and $4\text{-}NO_2\text{-}PhCH_2TeCN$ in more than 70 % yield. Yellow needles, m.p. ~120 °C (dec). (Found: C 58.76; H 4.09; N 4.45. Calc. for $C_{44}H_{36}BrN_3O_2P_2Te$: C 59.19; H 4.19; N 4.62). IR(KBr): As for I. UV(MeCN): A less distinct shoulder than for I at ~350 nm. NMR(MeCN): 4.40 (s, 2H).

III. $[PNP][4\text{-}NO_2\text{-}PhCH_2Te(CN)I]$. From 0.70 g (0.0027 M) $4\text{-}NO_2\text{-}PhCH_2I$ and 1.75 g (0.0025 M) [PNP]TeCN 1.92 g (80 %) was obtained as described for I. An identical product was prepared from $4\text{-}NO_2\text{-}PhCH_2TeCN$ and [PNP]I in aceto-

nitrile. Yellow-brownish needles, m.p. ~120 °C. (dec.) (Found: C 55.83; H 3.88; N 4.23. Calc. for $C_{44}H_{36}IN_3O_2P_2Te$: C 55.32; H 3.80; N 4.40). IR(KBr): As for I. UV(MeCN): No distinct shoulder in the 330–360 nm region; the spectrum appears as a smooth curve which above 360 nm is shifted some 15 nm toward higher wavelength as compared with the parent organic tellurocyanate but with a tail toward 450 nm. NMR(MeCN): 4.46 (s, 2H).

Instrumental. A Perkin-Elmer UV-VIS Spectrophotometer Model 555 was used for the UV measurements. A Perkin-Elmer 399 B Infrared Spectrophotometer was used for the recording of the IR spectra. The proton chemical shifts were determined with a Varian EM 360 A NMR Spectrometer at ~25 °C.

X-Ray data and structure determination. The crystals of I, II and III from acetone–diethyl ether were suitable for the X-ray study. An Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation was used for the determination of cell parameters, and for recording of intensity data. Cell parameters were in each case based upon least square fits to the diffractometer settings of 25 independent reflections ($\lambda(\alpha_1)=0.70926$ Å, $\lambda(\alpha_2)=0.71354$ Å).[10]

Intensity data ($\lambda=0.71073$ Å) were recorded at room-temperature using the ω-scan technique with variable scan speed; I: 0.8–4 min^{-1}; II: 0.8–2.5 min^{-1}; III: 1.7–7 min^{-1}. Minimum scan width was 1.5° including $2\times0.25°$ background scans. The orientation of the crystals was checked at intervals of 100 recordings. Three standard reflections were measured every 2 h and the intensity data later corrected according to the variation of these. Maximum corrections (average corrections in parentheses); I: 4 % (1 %); II: 8 % (3 %); III: 5 % (0 %). All crystallographically independent reflections with $\theta<25°$ were recorded.

The intensity data were corrected for Lorentz, polarization, and absorption effects. The absorption corrections were based on crystal faces and dimensions. The structure of I and III were solved by interpretation of Patterson and Fourier density maps. Since I and II are isomorphous, initial atomic coordinates for II were taken from I and showed to be satisfactory for the subsequent refinement.

Atomic form factors and anomalous dispersion

Table 1. Crystal data and structural parameters.

Compound	I	II	III
Mp. °C	~120(dec)	~120(dec)	~120(dec)
Recryst. from	Acetone/ether[a]	As I	As I
Cryst. system	Triclinic	Triclinic	Triclinic
a(Å)	9.833(2)	9.902(2)	12.578(2)
b(Å)	14.435(2)	14.464(2)	12.730(3)
c(Å)	16.307(2)	16.392(1)	14.258(2)
α(°)	66.09(2)	65.95(2)	77.68(2)
β(°)	78.63(2)	78.57(2)	79.05(2)
γ(°)	71.77(2)	71.97(2)	69.92(2)
Volume (Å^3)	2003.2(5)	2031.7(4)	2077.7(8)
Temp. °C	Room temp. (~19 °C)	As I	As I
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
M	863.80	908.25	955.25
Z	2	2	2
F(000)	872	908	944
D_c (gcm^{-3})	1.432	1.485	1.527
Abs. coeff. (cm^{-1})	9.595	19.23	16.12
Cryst.dim. (mm)	$0.23\times0.60\times0.07$	$0.23\times0.08\times0.05$	$0.1\times0.1\times0.2$
Fudge factor	0.020	0.020	0.020
Scale factor	1.9545	2.3566	0.6363
No. of refl.	7051	7142	7285
No. of refl. $>2\sigma$	3589	3166	5256
R	0.048	0.051	0.036
R_w	0.046	0.046	0.037
S	1.136	1.197	1.385
Diff. Four. max. eÅ^{-3}	0.21	0.23	0.46

[a] Diethyl ether.

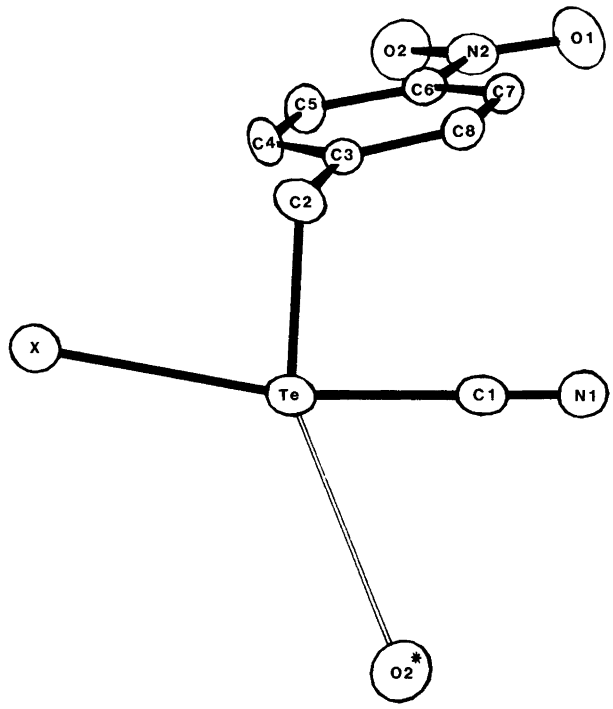


Fig. 1. ORTEP drawing of the $[4\text{-}NO_2\text{-}PhCH_2Te(CN)X]^-$-anion, *cf.* text. (When X = I no Te-O_2* bond is observed).

coefficients were taken from Ref. 11. Hydrogen atoms were placed geometrically at C–H = 0.95 Å and fixed, their thermal parameters refined and averaged, then attributed rounded values in the full matrix least square iterations to follow. The function minimized is $\Sigma\omega\Delta F^2$; the attributed weights correspond to the counting statistics plus 2 % of the net intensity (fudge factor of 0.02).

Reflections with $I < 2\sigma(I)$ were excluded and considered unobserved in the least square refinement.

All computer programs used belong to the Enraf-Nonius Structure Determination Pack, version 17-1980.

Table 1 summarizes the crystal data and other relevant information. Final atomic coordinates together with tables of observed and calculated structure factors are available from the authors, and have been made available to the crystallographic Data Center at Cambridge (GB).

RESULTS

An ORTEP drawing of the anion in I, the $[4\text{-}NO_2\text{-}PhCH_2Te(CN)Cl]$-anion, including numbering of the atoms, is shown in Fig. 1. For clarity the hydrogen atoms are omitted. In this drawing the tellurium atom, Te, the cyano carbon, C1, and the methylene carbon atom, C2, are in the plane of the paper. Since the anions in the two isomorphous compounds, I and II, are most similar except for the Te–Cl and the Te–Br bond distances, the drawing in Fig. is representative also for the $[4\text{-}NO_2\text{-}PhCH_2Te(CN)Br]$-anion and the halogen atom is therefore termed X.

In these two anions the tellurium atom forms a weak intermolecular "secondary bond"[12] to an oxygen atom, O2*, from a neighbouring nitro group of 3.449(5) Å (I) and 3.435(7) Å (II). In the anion of III, the $[4\text{-}NO_2\text{-}PhCH_2Te(CN)I]$-anion, no such weak intermolecular bond to an oxygen atom or to any other atom (< 4.5 Å) could be observed. In this anion the tellurium atom is thus strictly three-coordinated. The rest of the anion, however, is most similar to the anions in I and II. With the exception of the weak Te–O2* interactions as shown in Fig. 1, Fig. I may thus also illustrate the anion in III. In the accompanying table to Fig. 1, Table 2, the

Table 2. Distances of the various atoms from the C1 – Te – C2-plane in the anions as shown in Fig. 1 together with bond lengths and bond angles for the tellurium part of the anions.

	I	II	III
Distance from C1TeC2-plane (Å)			
X	−0.342(2)	−0.392(1)	−0.230(0)
O2*	+0.958(6)	+0.984(7)	
N1	−0.099(8)	−0.077(10)	−0.046(5)
C3	−1.293(7)	−1.319(9)	−1.341(4)
C4	−2.368(8)	−2.365(10)	−2.350(4)
C5	−3.616(8)	−3.623(10)	−3.567(5)
C6	−3.781(7)	−3.775(9)	−3.768(4)
C7	−2.745(7)	−2.728(9)	−2.790(5)
C8	−1.502(8)	−1.500(10)	−1.579(5)
N2	−5.108(6)	−5.114(8)	−5.064(4)
O1	−5.237(6)	−5.206(8)	−5.223(4)
O2	−6.047(6)	−6.031(7)	−5.914(4)
Bond lengths (Å)			
Te – X	2.923(2)	3.100(1)	3.299(0)
Te – Cl	2.140(10)	2.130(12)	2.144(5)
Te – C2	2.159(8)	2.155(10)	2.154(4)
Te – O2*	3.449(5)	3.435(7)	
C1 – N1	1.128(10)	1.120(12)	1.086(5)
Bond angles (°)			
C1 – Te – C2	87.4(3)	87.8(4)	88.7(2)
X – Te – C1	167.9(2)	167.6(3)	170.9(1)
X – Te – C2	82.5(2)	82.2(3)	83.1(1)
X – Te – O2*	122.8(7)	120.2(1)	
C1 – Te – O2*	68.7(2)	71.5(3)	
Te – C1 – N1	174.8(9)	176.0(10)	176.5(5)
Te – C2 – C3	110.6(5)	110.8(6)	112.5(2)

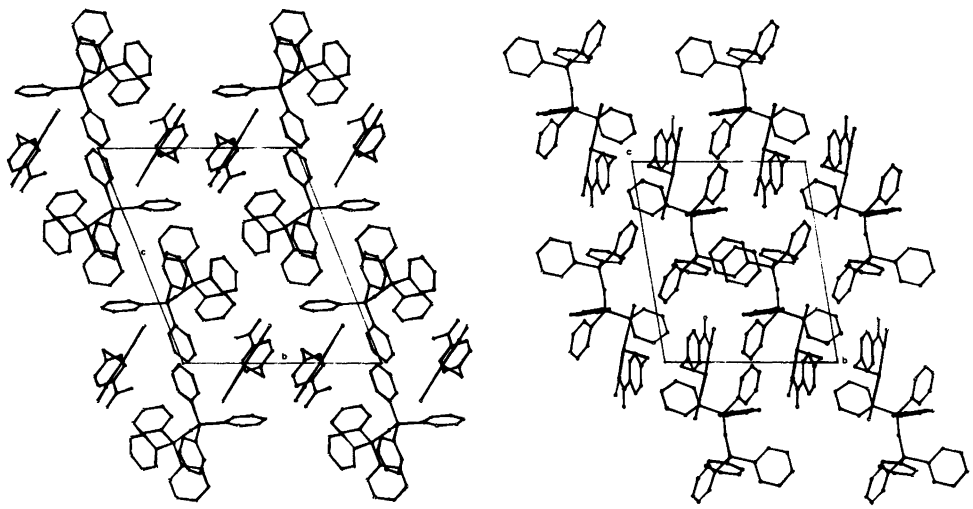
distances of the various atoms from the C1TeC2-plane for all three anions are listed together with the bond lengths and the bond angles which characterize the coordination of the tellurium atoms. The structural data for the remaining part of the anions, the 4-nitrobenzyl part, are listed in Table 3. Fig. 2 shows the projections of the unit cells along the *a*-axes for I and III.

The phenyl rings in the anions and in the cations are all planar within experimental error. In all three anions, particularly in the anions in I and II, the methylene carbon atom, C2, and the nitrogen atom, N2, do not lie in the plane of the phenyl ring. The distances of these two atoms and of the oxygen atoms, O1 and O2, from the plane formed by the phenyl carbon atoms, C3 to C8, are summarized in Table 4. In the anions the C6N2O1O2 part is planar within experimental error. In I and II the nitro group is bent out of the phenyl plane toward the tellurocyanate group by 2.8 and 3.0°, respectively, but is not twisted. In III the nitro group is not bent out of this phenyl plane but is slightly twisted, 0.7°; *cf.* Table 4.

Conformationally the three anions are quite similar; *cf.* Fig. 3 which shows general Newman projections for the three anions along the Te – C2 bond and along the C2 – C3 and the C3 – C6 bonds. For clarity of the latter projection, the distance of C2 from the phenyl plane is disregarded and the nitro group in the rear of the phenyl ring is omitted.

Table 3. Structural data for the 4-nitrobenzyl part of the anions.

	I	II	III
Bond lengths (Å)			
C2–C3	1.466(10)	1.501(12)	1.503(5)
C3–C4	1.394(10)	1.374(12)	1.376(5)
C4–C5	1.375(10)	1.393(13)	1.372(5)
C5–C6	1.370(10)	1.359(13)	1.375(5)
C6–C7	1.360(9)	1.371(12)	1.365(6)
C7–C8	1.382(10)	1.369(12)	1.374(6)
C8–C3	1.388(9)	1.377(12)	1.382(5)
C6–N2	1.471(9)	1.486(11)	1.476(5)
N2–O1	1.211(8)	1.215(10)	1.208(5)
N2–O2	1.228(8)	1.212(9)	1.200(5)
Bond angles (°)			
C2–C3–C4	120.9(7)	119.3(9)	121.1(3)
C3–C4–C5	121.9(7)	119.9(9)	121.3(4)
C4–C5–C6	118.3(7)	119.1(9)	118.8(4)
C5–C6–C7	122.0(7)	121.6(9)	121.4(4)
C6–C7–C8	119.3(7)	119.1(9)	119.1(4)
C7–C8–C3	120.9(7)	120.7(9)	120.9(4)
C8–C3–C2	121.6(7)	121.1(9)	120.3(4)
C8–C3–C4	117.5(7)	119.5(9)	118.6(4)
C5–C6–N2	120.1(7)	120.3(9)	119.4(4)
C7–C6–N2	118.0(7)	118.1(9)	119.2(4)
C6–N2–O1	119.1(7)	117.8(9)	117.7(5)
C6–N2–O2	117.9(7)	117.0(10)	118.0(4)
O1–N2–O2	122.9(8)	125.2(10)	124.1(5)



I III

Fig. 2. The projection of the unit cell along the *a*-axes for I (left) and for III (right).

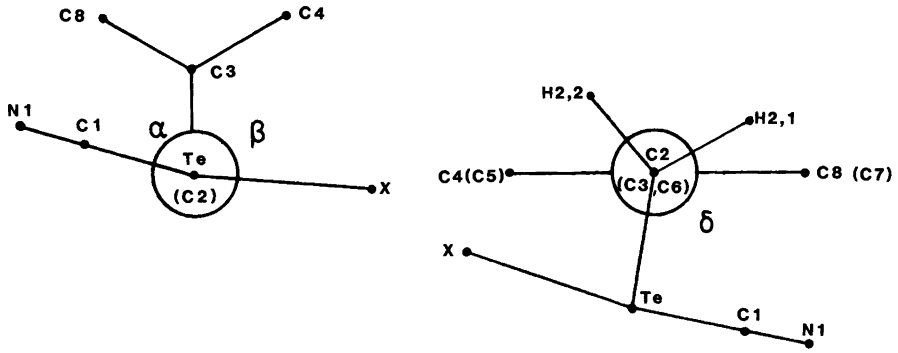
Table 4. The distance of C2, N2, O1 and O2 from the phenyl ring plane. Negative value is defined as the same side as the [Te(CN)X]-part of the anions, *cf.* Fig. 1.

	I	II	III
C2	−0.108(8)	−0.104(10)	+0.035(4)
N2	−0.076(6)	−0.081(8)	+0.020(4)
O1	−0.113(6)	−0.111(8)	−0.016(4)
O2	−0.128(6)	−0.110(7)	+0.010(5)

DISCUSSION

The UV and the ^1H NMR spectra, *cf.* Experimental, readily suggest that products are formed when ionic halides are added to an organic tellurocyanate, RTeCN, in solution. The present crystallographic study serves as the final proof for the existence of complex anions of the general type $[RTe(CN)X]^-$. A number of experiments were performed during the present study in order to prepare similar anions from various alkyl selenocyanates, RSeCN, by varying the cation, n-But_4N^+, Ph_4As^+ or $[PNP]^+$, and also the solvent. However, all attempts failed and not even spectroscopic evidence for any interaction between RSeCN and X^- could be obtained. Apparently, the formation and existence of $[RTe(CN)X]^-$ is unique for tellurium in the *VI* main group. Presumably, the ability of this element to make very stable Te(II)-complexes is the cause for this observation, complexes in which the bonding in the linear three-center system is of the two-electron type.[13]

Bonding to the tellurium atom in the anions. In all the three anions the halogen atom is approximately *trans* to the cyano group with X−Te−Cl bond angles of 167.9(2)°(I), 167.6(3)°(II) and 170.9(1)°(III). This observation is as anticipated in view of the *trans* effect of the 4-nitrobenzyl group, particularly its *σ-trans* effect, which is known to be far greater than that of the cyano group.[14] Due to this bonding between the central tellurium atom and the halogen



	I	II	III	RTeCN[6]
α°	70.5	70.1	74.9	77.4
β°	102.8	102.6	101.0	
δ°	96.7	97.2	100.1	98.0

Fig. 3. General Newman projections for the anions in I, II and III; along the Te−C2 bond (left) and along the C2−C3 and the C3−C6 bond (right).

Table 5. A comparison between the Te–X bond distances in $[RTe(CN)X^-]^-$, $Te-X_{obs}$, with the sum of the van der Waals' radii of tellurium and the halogens, ΣR_{vdW}, and the sum of the covalent single bond distances, ΣR_{cov}. (Bond distances in Å.)

	I(X = Cl)	II(X = Br)	III(X = I)
ΣR_{vdW}	3.81	3.91	4.04
ΣR_{cov}	2.31	2.43	2.60
$Te-X_{obs}$	2.923(2)	3.100(1)	3.299(0)
$\Sigma R_{vdW}-(Te-X)_{obs}$	0.89	0.81	0.74
$(Te-X)_{obs}-\Sigma R_{cov}$	0.61	0.67	0.70

atoms *trans* to the cyano group, the Te–C(CN) bond lengths are significantly elongated from what was observed in the parent organic tellurocyanate, 2.060(4) Å,[6] to 2.140(10) Å in I, 2.130(12) in II and 2.144(5) Å in III. Actually, this elongation of the Te–C(CN) bond causes the two Te–C bonds in the anions, the Te–C(CN) bond and the Te–$C(CH_2)$ bond, to be fairly similar, 2.13–2.16 Å, when taking the experimental uncertanties into account, *cf.* Table 2. This range is the expected one for tellurium–carbon single bonds.[15] Significantly shorter Te–C bond lengths as in 4-nitrobenzyl tellurocyanate[6] have been observed in the tellurocyanate ion,[16] in phenoxatellurine[17] and especially in Te=C=S.[18]

A comparison is given in Table 5 between the Te–X bond lengths in the anions and the sum of the covalent single bond distances, ΣR_{cov}, and the sum of the van der Waals' radii, ΣR_{vdW}.[12,19] The Te–X bond distances in the anions are clearly significantly longer than Te–X single bonds by 0.6 to 0.7 Å but are from 0.7 to 0.9 Å shorter than the sum of the van der Waals' distances. It is notable that the Te–Cl bond length is closer to ΣR_{cov} and further from ΣR_{vdW} than is the length of the Te–I bond. This suggests the bond order of the Te–X bonds in the anions to be Te–Cl > Te–Br > Te–I, a bond order sequence which at first sight is surprising in view of the fact that Te(II) is a typical soft acid.[13,20] However, since the halogen atoms are *trans* to a very electronegative group, the cyano group, the more electronegative halogen will be favoured. Apparently, symbiosis[21] has to be taken into account when considering bonding in Te(II)-complexes. When halogen atoms are linked to Te(II) *trans* to a soft atom as in PhTe(tu)X (tu = thiourea) the bond prder is the expected one, Te–I > Te–Br > Te–Cl.[22] Owing to the strength of the Te–I bond in these Te(II)-complexes the *trans*-bond-lengthening effect upon the Te–S bond of iodine is superior to that of bromine and chlorine causing the Te–S bond length in PhTe(tu)I to be ~0.09 Å longer than in the corresponding chloro and bromo compounds.[22] As mentioned above, the Te–C(CN) bonds in the $[4\text{-}NO_2\text{-}PhCH_2Te(CN)X]^-$ anions are independent upon the halogen atom when taking the experimental error into account, *cf.* Table 2.

In spite of the apparent weakness of the Te–I bond in the anion in III, the iodine atom in this anion is closer to the C2TeCl plane than are the chlorine atom and the bromine atom in I and II, respectively; *cf.* Fig. 1 and Table 2, first entry. The anion in III is thus closer to an idealized T-shaped anion than are the anions in I and II. In I and II the tellurium atom may be considered as tetracoordinated owing to the closeness of an oxygen atom from a neighbouring nitro group, *cf.* Fig. 1. Presumably the electronegativity of the chlorine and the bromine atoms will cause some positive charge to reside on the central tellurium atom enabling this atom to interact with the slightly negatively charged oxygen atoms. It should be emphasized, however, that this interaction is very weak; the observed bond distances of 3.449(5) Å (I) and 3.435(7) Å (II) are only slightly less than the van der Waals distance, 3.58 Å.[19] Furthermore, the oxygen atoms are close to 1 Å away from the C1TeC2 plane, *cf.* Table 2. It is notable, however, that the C1TeO2* bond angles in I and II, 68.7 and 71.5°, are most similar to the corresponding bond angle in 4-nitrobenzyl tellurocyanate, 68.9°, in which a considerably shorter Te–O* bond distance of 3.182(3) Å is observed.[6] In III, the iodo compound, the anion is strictly three-coordinated. In this respect this anion resembles PhTe(tu)I;[22] the corresponding chloro and bromo compounds are tetracoordinated in the solid state.[22]

The bond angles around the tellurium atom are in the three anions most similar, *cf.* Table 2. The

C1–Te–C2 bond angles are slightly but significantly smaller by 2–3° than in the parent organic tellurocyanate in which this bond angle is 90.6°.[6] Presumably, this bond angle decrease is caused by repulsion between the lone pairs on the tellurium atom in accordance with the VSEPR theory.[23] The same argument applies to the X–Te–Cl bond angles which in all three anions are significantly less than 180°.

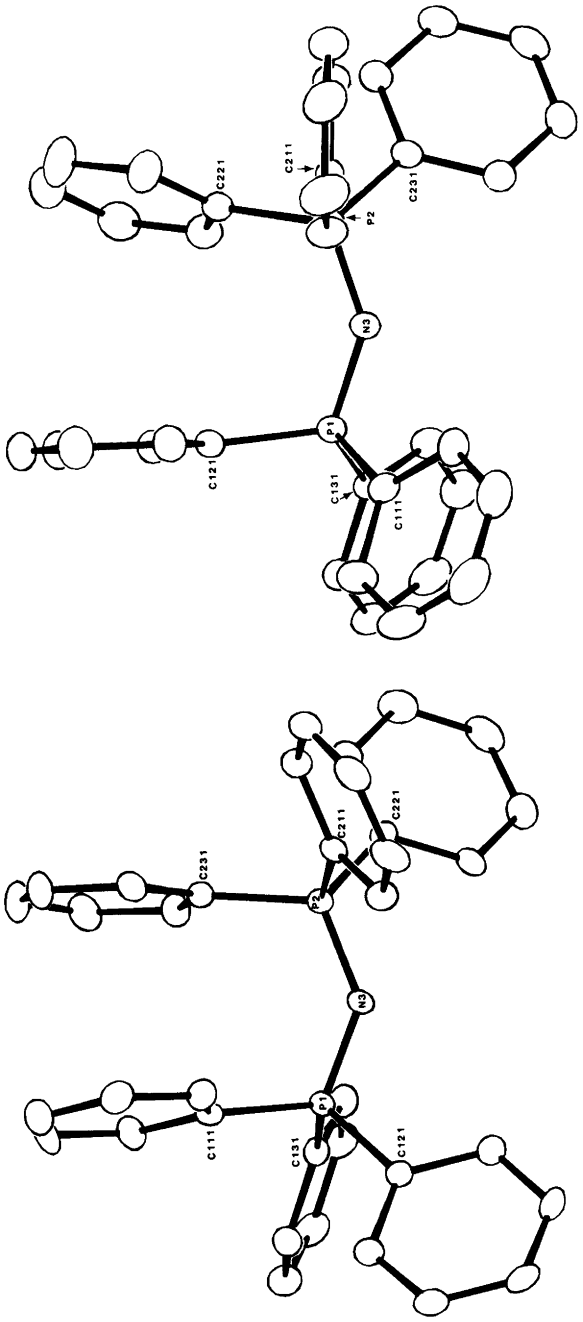
The TeCN group. As mentioned above the Te–C(CN) bonds are longer in the anions than in the organic tellurocyanate from which they are derived.[6] This elongation appears to be accompanied by a slight but distinct deviation from linearity of the TeCN group; the Te–C1–N1 bond angles being 174.8(9)° in I, 176.0(10)° in II, 176.5(5)° in III as compared with 179.3(4)° in 4-nitrobenzyl tellurocyanate.[6] In all three anions, and especially in the anions of I and II, the N1-nitrogen atom is significantly below the C1–Te–C2 plane; *cf.* Fig. 1 and Table 2. The C1–Te–C2 plane and the Te–C1–N1 plane are almost perpendicular in all three anions.

The non-linearity of the TeCN groups in the anions is small and may be caused by packing effects, but it is interesting in view of the fact that numerous examples of bent SCN groups are known, both in inorganic[24] and in organic compounds.[25] This non-linearity of the thiocyanate group has been suggested to be due to some contribution of the $-S=C=N$ form giving rise to fairly short S–C bond lengths. For a critical survey of bonding in the thiocyanate group, *cf.* Ref. 26. The anticipated elongation of the C–N bond has not been observed.

Actually, in the three anions the opposite appears to be the case with fairly long Te–C1 bond lengths and short C1–N1 bond lengths, especially in III. A very short C1–N1 bond length, significantly less than the accepted C1–N1 bond length of 1.14–1.15 Å has previously been observed in the tellurocyanate ion.[16] This raises the general question whether the short C1–N1 bond length, ~1.09 Å, as observed in the [4-NO_2PhCH_2Te(CN)I]-anion and in the $TeCN^-$ anion[16] is real or is a result of the experimental method. For a detailed discussion regarding the electron density in a linear molecule and the effect of thermal vibration upon bond lengths, *cf.* Ref. 27. Presently, it seems as if a critical discussion of bond angles and bond lengths in the tellurocyanate group has to be postponed until low-temperature data are made available.

Table 6. Structural data for the $[Ph_3P-N-PPh_3]^+$-cations.

	I	II	III
Bond lengths (Å)			
N3–P1	1.581(5)	1.581(6)	1.578(3)
N3–P2	1.581(5)	1.576(6)	1.569(3)
P–C	1.796	1.794	1.798
C–C	1.385		
Bond angles (°)			
P1–N3–P2	137.1(4)	136.8(4)	142.8(2)
C111–P1–C121	107.7(3)	106.4(4)	107.2(2)
C111–P1–C131	107.7(3)	107.9(4)	107.9(2)
C121–P1–C131	107.4(3)	107.5(4)	107.6(2)
C211–P2–C221	108.7(3)	108.7(4)	108.3(2)
C211–P2–C231	107.6(3)	107.2(4)	106.7(2)
C221–P2–C231	108.0(3)	107.4(4)	106.4(2)
N3–P1–C111	113.8(3)	114.5(4)	108.7(2)
N3–P1–C121	107.7(3)	107.7(4)	115.2(2)
N3–P1–C131	112.2(3)	112.5(4)	110.0(2)
N3–P2–C211	110.3(3)	110.7(4)	114.7(2)
N3–P2–C221	107.8(3)	108.3(4)	111.7(2)
N3–P2–C231	114.2(3)	114.4(4)	108.7(2)
C–P–C	107.8	107.5	107.4
N–P–C	111.0	111.3	111.5



I III

Fig. 4. ORTEP drawing of the $[PNP]^+$-cations in I (left) and in III (right). The P1, the N3 and the P2 atoms are in the plane of the paper.

The Newman projections in Fig. 3 clearly indicate that the TeCN-group is *synclinal (gauche)* to the C2–C3 bond in all three anions. The torsion angle is in all anions most similar to the one observed in the parent organic tellurocyanate, 77.4°.[6] Fig. 3 shows that the TeC2C3 planes make angles of ~ 100° with the benzene ring in all three anions which is quite comparable with the corresponding angle in 4-nitrobenzyl tellurocyanate, 98.0°.[6] It is apparent that no significant conformational changes take place when 4-nitrobenzyl tellurocyanate is complexed with halide ions.

The 4-nitrobenzyl group. All bond lengths and bond angles as listed in Table 3 are as expected. The C2–C3 bond length in the anion of I is fairly small but we cannot offer a satisfactory explanation for this observation. The N–O bond lengths and the C6–N–O bond angles in the anions of I and II are similar since the intermolecular contact between the tellurium atom and O2 is very weak. This observation contrasts what was found in the case of 4-nitrobenzyl tellurocyanate.[6]

The $[PNP]^+$-cations. ORTEP drawings of the cations in I and III together with naming of the central atoms are shown in Fig. 4. Table 6 summarizes the most important structural data for the cations in the three salts. The P1 – N3 – P2 bond angle in III is seen to be significantly larger than in I and II, *cf.* Table 6. However, bond angles in this cation, when bent, are known to range from 135 to 145° depending upon packing. The C–P–C bond angles in the cations are close to an average value of 107.5°. The cations are less symmetrical with regard to the N–P–C bond angles which range from 107 to 115° with an average value of 111.3°.

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