Journal of Organometallic Chemistry, 281 (1985) 205–211
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TELLURATED AZOBENZENES: THE CRYSTAL AND MOLECULAR STRUCTURE OF (2-PHENYLAZOPHENYL-*C*,*N*′)TELLURIUM(IV) TRICHLORIDE

MOHAMMED A.K. AHMED, WILLIAM R. McWHINNIE,

Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET (Great Britain)

and THOMAS A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT (Great Britain)

(Received August 8th, 1984)

Summary

The preparation of the title compound via a *trans*-metallation route has been reinvestigated, and also its formation by direct telluration of azobenzene at 135–150°C has been demonstrated. ^{13}C NMR data for tellurated and mercurated azobenzene are compared. Reduction with excess hydrazine affords the new ditelluride $(C_{12}H_9N_2)_2Te_2$.

The crystal structure of (2-phenylazophenyl-*C*,*N*′)tellurium(IV) trichloride has been determined. The coordination about Te is octahedral with a vacant equatorial position, two Cl atoms apical, the third Cl atom and the bidentate organic ligand equatorial. The title compound is essentially monomeric, there are no significant interactions between Te and Cl in neighbouring molecules.

Introduction

The first tellurated derivatives of azobenzene were reported in 1979 [1]. The acount detailed the preparation and physical properties of some tellurium(IV) derivatives and included a structural determination of (2-phenylazophenyl-*C*,*N*′)tellurium(II) chloride which was, one of the first compounds containing an intramolecular Te–N bond to be crystallographically characterised.

We recently decided to extend the known range of tellurated azobenzenes and, to that end, required (2-phenylazophenyl-*C*,*N*′)tellurium(IV) trichloride as a starting material. In new hands the original synthesis did not seem to proceed exactly as reported [1], hence it seemed sensible to probe the preparation more deeply and also to investigate further the possibility of the direct metallation of azobenzene with tellurium.

0022-328X/85/$03.30

To establish beyond doubt that (2-phenylazophenyl-*C,N′*)tellurium(IV) trichloride had been prepared, the crystal and molecular structure was determined. This determination is timely in view of recent structural interest in organotellurium(IV) trihalides [2–8] and organotetrahalotellurates(IV) [9].

Experimental and results

Synthesis

(2-Phenylazophenyl-C,N′)tellurium(IV) trichloride. The synthesis was carried out, as reported previously [1], via a *trans*-metallation reaction with (2-phenylazophenyl-*C,N′*)mercury(II) chloride [10]. The reaction proceeded as reported by Musa [11] until the final stage when, in addition to the orange product reported, it was noted that the white crystals of $HgCl_2 \cdot (dioxane)_2$ were heavily contaminated with dark, almost black, well formed crystals of another substance which could be separated from the mercury complex by dissolution of the latter in methanol. The black material, which was orange-yellow when finely ground was pure $(C_{12}H_9N_2)TeCl_3$. Recrystallisation of the orange product from nitromethane gave a mixture of orange and black crystals. Treatment with methanol left the black material (pure trichloride) and evaporation of methanol gave the orange product.

The orange product gave an analysis that was close to that expected for the trichloride, but the figures fluctuated over a few percent from preparation to preparation. However reduction of both the orange and black materials with hydrazine [1] gave pure (2-phenylazophenyl-*C,N′*)tellurium(II) chloride, m.p. 125°C. The literature m.p. was 80°C but the discrepancy is not as worrying as may appear since others have informed us that a crystallographically characterised polymorphous form of this material exists [12], also the earlier sample has been crystallographically characterised.

We believe that the orange material is essentially (2-phenylazophenyl-*C,N′*)tellurium(IV) trichloride which is slightly contaminated with the rather soluble (2-phenylazophenyl-*C,N′*)mercury(II) chloride. This would explain the fluctuating analysis, the fact that the m.p. reported by Musa was 235°C as opposed to 244–245°C for the black material, and the chemical behaviour on hydrazine reduction.

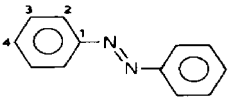
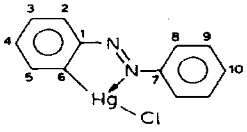
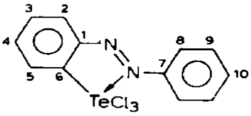
Given the identification of these problems it seemed desirable to confirm the identity of (2-phenylazophenyl-*C,N′*)tellurium(IV) trichloride by ^{13}C NMR and X-ray crystallographic studies. Found: C, 35.0; H, 2.00; N, 6.75; Cl, 25.1. $C_{12}H_9Cl_3N_2Te$ calcd.: C, 34.7; H, 2.17; N, 6.75; Cl, 25.7%.

(2-Phenylazophenyl-C,N′)tellurium(IV) trichloride by direct reaction of azobenzene and tellurium tetrachloride. Tellurium tetrachloride (5.39 g, 0.02 mol) and azobenzene (21.84 g, 0.12 mol) were heated together under dinitrogen, the temperature of the stirred mixture being maintained in the range 135–150°C. When evolution of HCl ceased, the mixture was cooled to $< 100°C$ and methanol was added to dissolve excess azobenzene. The precipitate was then washed with methanol until colourless washings were obtained. The precipitate was shown by analysis and ^{13}C NMR to be $(C_{12}H_9N_2)TeCl_3$. Yield 40%. Found: C, 34.6; H, 2.10; N, 6.85; Cl, 25.9%.

Bis(phenylazophenyl-C,N′)ditelluride. Hydrazine hydrate (1.9 g, 0.038 mol) in ethanol (8 cm^3) was added very slowly to a refluxing mixture of (phenylazophenyl-*C,N′*)tellurium(IV) trichloride (2.08 g, 0.005 mol) and ethanol (38 cm^3). Initially,

TABLE 1

^{13}C NMR DATA IN DMSO-d_6; (ppm, vs. Me_4Si)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
	151.8	122.4	129.2	131.3						
	154.2 [a]	122.6	129.1	131.7	137.7	143.1	150.9	127.4	129.5	132.2
	150.3	123.3	130.9	134.8	137.2	139.5	145.8	129.3	133.6	135.6

[a] $J(^{199}Hg-^{13}C)$ 2333 Hz.

TABLE 2

FRACTIONAL ATOMIC COORDINATES WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Te(1)	0.22689(3)	0.14123(3)	0.24503(3)
Cl(1)	0.1910(2)	0.2286(2)	0.4990(1)
Cl(2)	0.2825(2)	0.0273(2)	−0.0040(2)
Cl(3)	0.3487(2)	0.4314(2)	0.2771(2)
N(1)	0.1775(5)	−0.1393(5)	0.2302(4)
N(2)	0.3036(5)	−0.1642(6)	0.2604(4)
C(1)	0.4510(6)	−0.0173(7)	0.3059(5)
C(2)	0.4553(6)	0.1373(7)	0.3118(5)
C(3)	0.5998(7)	0.2773(8)	0.3607(6)
C(4)	0.7436(7)	0.2578(9)	0.4036(6)
C(5)	0.7392(7)	0.1057(10)	0.3973(6)
C(6)	0.5917(7)	−0.0378(9)	0.3458(6)
C(7)	0.0237(6)	−0.2803(6)	0.1875(5)
C(8)	−0.1129(7)	−0.2560(7)	0.1420(6)
C(9)	−0.2640(7)	−0.3916(9)	0.0954(7)
C(10)	−0.2782(8)	−0.5426(8)	0.0961(6)
C(11)	−0.1412(9)	−0.5621(8)	0.1449(7)
C(12)	0.0136(7)	−0.4301(7)	0.1896(1)
H(3)	0.6003	0.3999	0.3726
H(4)	0.8587	0.3702	0.4486
H(5)	0.8366	0.0832	0.4235
H(6)	0.5877	−0.1625	0.3359
H(8)	−0.0992	−0.1397	0.1460
H(9)	−0.3612	−0.3639	0.0653
H(10)	−0.3830	−0.6510	0.0539
H(11)	−0.1401	−0.6764	0.1400
H(12)	0.1277	−0.4457	0.2251

each addition was accompanied by the vigorous evolution of dinitrogen and the trichloride gradually dissolved. On completing the addition, and when no further dinitrogen was evolved, the mixture was cooled to 0°C to give a golden brown precipitate which was filtered, washed with methanol and dried in a vacuum desiccator to m.p. 134°C. (Yield 65–70%). Found: C, 46.7; H, 2.90; N, 8.85. $C_{24}H_{18}N_4Te_2$ calcd.: C, 46.7; H, 2.92; N, 9.07%.

Physical measurements

Infrared spectra were determined with a Perkin–Elmer 599 instrument. Spectra were in accord with expectation [1,11]. ^{13}C NMR spectra were determined with a Jeol FX90Q instrument. The products from *trans*-metallation and from the direct telluration of azobenzene gave identical ^{13}C NMR spectra. Table 1 reports some data, chemical shifts are reported with regards to Me_4Si.

Elemental analysis was by the Analytical Services Section, Chemistry Department, University of Aston.

X-Ray structure analysis of (phenylazophenyl-C,N')tellurium(IV) trichloride. Cell

TABLE 3

BOND DISTANCES (Å), ANGLES (°) AND TORSION ANGLES (°).

Te–Cl(1)	2.483(1)	C(6)–C(1)	1.382(7)
Te–Cl(2)	2.491(1)	C(1)–N(2)	1.423(7)
Te–Cl(3)	2.406(2)	N(2)–N(1)	1.255(6)
Te–N(1)	2.417(4)	N(1)–C(7)	1.431(7)
Te–C(2)	2.114(5)	C(7)–C(8)	1.390(8)
C(1)–C(2)	1.390(8)	C(8)–C(9)	1.392(8)
C(2)–C(3)	1.374(8)	C(9)–C(10)	1.359(11)
C(3)–C(4)	1.413(9)	C(10)–C(11)	1.382(11)
C(4)–C(5)	1.365(11)	C(11)–C(12)	1.399(8)
C(5)–C(6)	1.405(9)	C(12)–C(7)	1.363(8)
Cl(1)–Te–Cl(2)	171.7(1)	C(5)–C(6)–C(1)	117.4(6)
Cl(1)–Te–Cl(3)	93.0(1)	C(6)–C(1)–C(2)	121.7(5)
Cl(2)–Te–Cl(3)	92.3(1)	C(6)–C(1)–N(2)	115.3(5)
N(1)–Te–Cl(1)	87.0(1)	C(2)–C(1)–N(2)	123.1(4)
N(1)–Te–Cl(2)	86.3(1)	C(1)–N(2)–N(1)	113.6(5)
N(1)–Te–Cl(3)	165.2(1)	N(2)–N(1)–Te	115.3(3)
C(2)–Te–Cl(1)	86.3(1)	C(7)–N(1)–Te	128.0(3)
C(2)–Te–Cl(2)	87.0(1)	C(7)–N(1)–N(2)	116.7(5)
C(2)–Te–Cl(3)	92.9(1)	C(8)–C(7)–N(1)	116.1(5)
C(2)–Te–N(1)	72.3(2)	C(12)–C(7)–N(1)	121.5(5)
C(1)–C(2)–C(3)	121.0(5)	C(12)–C(7)–C(8)	122.4(5)
C(1)–C(2)–Te	115.6(4)	C(9)–C(8)–C(7)	118.0(6)
Te–C(2)–C(3)	123.4(4)	C(10)–C(9)–C(8)	121.0(7)
C(2)–C(3)–C(4)	117.6(6)	C(11)–C(10)–C(9)	119.8(6)
C(3)–C(4)–C(5)	121.3(6)	C(12)–C(11)–C(10)	120.8(6)
C(4)–C(5)–C(6)	121.0(5)	C(11)–C(12)–C(7)	117.9(6)
C(2)–C(1)–N(2)–N(1)	−2.0(7)		
C(7)–N(1)–N(2)–C(1)	−178.1(7)		
C(6)–C(1)–N(2)–N(1)	177.3(7)		
N(2)–N(1)–C(7)–C(12)	4.3(7)		
N(2)–N(1)–C(7)–C(8)	−174.1(7)		

parameters and reflection intensities were measured from a prism-like crystal 0.45 × 0.43 × 0.15 mm using an Enraf–Nonius CAD-4 diffractometer as described previously [13]. 2640 reflections were scanned in the range $2 < \theta < 25°$. Two standard reflections remeasured every 2 h showed no significant variation. Lorentz and polarisation factors were applied; 2289 unique reflections $[F > 5\sigma(F)]$ were considered observed and were used in the structure analysis.

Crystal data. $C_{12}H_9N_2TeCl_3$, $M = 415.1$, triclinic, space group $P\bar{1}$, a 8.734(2), b 9.219(3), c 10.363(3) Å, α 113.75(2), β 91.20(2), γ 109.26(2)°, U 709.49 A^3, $Z = 2$, D_m 1.93 g cm^{-3} (by flotation in bromoform/carbon tetrachloride), D_c 1.945 g cm^{-3}, $F(000) = 396$, μ(Mo-K_α, λ 0.71069 Å) 2.48 mm^{-1}.

The structure was solved by Patterson and Fourier methods. Following least squares refinement, first with isotropic temperature factors and then anisotropically, hydrogen atoms were located from a difference map but not refined. The calculations were terminated when all shifts were less than 0.10σ and R and R_w 0.0506 and 0.0674 respectively with $\omega = 1/[\sigma^2(F) + 0.005F^2)$.

Computations were carried out largely with SHELX [14]. Atomic coordinates are given in Table 2. Bond distances and angles are given in Table 3. Structure factors and thermal parameters are available from the authors.

Discussion

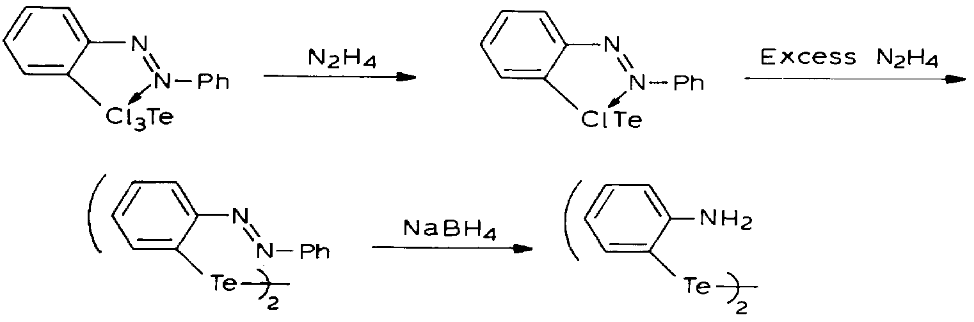
The preparation of (phenylazophenyl-C,N')tellurium(IV) trichloride by *trans*-metallation is slightly more complex than had previously seemed to be the case [1]; all physical data previously reported for the compound are valid and were reproduced in this study.

Although many reactions of $TeCl_4$ with aromatic compounds are believed to involve the electrophile $(TeCl_3)^+$, it was surprising that the direct telluration of azobenzene was not observed [11]. We now find that, by using more forcing conditions (135–150°C), for the reaction of $TeCl_4$ with molten azobenzene under dinitrogen that the tellurated compound is formed in moderate yield. The material produced by this route gave m.p., IR and ^{13}C NMR spectra identical with those obtained for the material produced via *trans*-metallation.

The ^{13}C NMR data are given in Table 1 and nicely confirm the telluration. The spectrum of $(C_{12}H_9N_2)HgCl$ is included for comparison. The greater solubility of the mercury compound allowed the observation of $^1J(^{199}Hg-^{12}C)$ (2333 Hz), but the one bond coupling to ^{125}Te could not be extracted from the random noise. As might be anticipated, the tellurium(IV) and mercury(II) spectra are very similar. One point of interest is that the carbon resonances of the "free" phenyl-ring are clearly more sensitive to the presence of tellurium than to that of mercury. This may imply a stronger coordinate interaction of the azo-nitrogen atom with tellurium(IV) than with mercury(II).

It is known that hydrazine reduction of $(C_{12}H_9N_2)TeCl_3$ will give $(C_{12}H_9N_2)TeCl$, and that use of $NaBH_4$ as reducing agent will afford bis(*o*-aminophenyl)ditelluride [1]. It seemed probable that the latter compound arose from bis(phenylazophenyl-C,N')ditelluride as implied in Scheme 1. We now find that treatment of $(C_{12}H_9N_2)TeCl_3$ with an excess of hydrazine does indeed produce the ditelluride thus completing the series.

SCHEME 1. Reduction sequence for (phenylazophenyl-*C*,*N*′)tellurium(IV) trichloride



The crystal and molecular structure of (phenylazophenyl-C,N′)tellurium(IV) trichloride

The structure of the complex and the atom numbering are shown in Fig. 1. The coordination about tellurium can be considered as essentially octahedral with a lone pair of electrons occupying the fourth equatorial site. The whole molecule apart from the apical chlorine atoms, Cl(1) and Cl(2), is planar to within ±0.07 Å. Cl(1) and Cl(2) lie 2.48 Å on either side of the molecular plane. The organic ligand's deviation from planarity is illustrated by the torsion angles listed in Table 3, the major component being a twist of ca. 5° of the free phenyl ring around C(7)–N(1).

The distortions of the coordination geometry from ideal octahedral values, particularly N(1)–Te–Cl(3) (165.2°) can be explained in terms of a lone pair of electrons occupying an equatorial position between N(1) and Cl(3). The small value of the angle N(1)–Te–C(2) (72.3°) and somewhat large value of the angle Cl(3)–Te–C(2) (92.9°) are due to constraints arising from the five-membered chelate ring. The axial atoms are displaced away from the lone pair electrons reducing the Cl(2)–Te–Cl(1) angle to 171.7° from an ideal value of 180°.

The distance Te–C(2) (2.114 Å) is in good agreement with the sum of the Pauling [15] single bond covalent radii of Te (1.37 Å) and sp^2-hybridised carbon (0.74 Å), and with values in the crystal structures of the analogous compounds, $PhTeCl_3$ [8,16], (4-$EtOPhTeCl_3$) [17] and $(C_7H_7O)_2TeCl_2$ [18], range 2.09–2.13 Å. The Te–N distance (2.417 Å) is much larger than the sum of the covalent radii (2.07 Å) [15], but is close to the value in the crystal structure of $(C_9H_8NO_2)TeCl_3$ (2.402 Å) [7]. The Te–Cl distances (2.406 Å, equatorial, 2.483 and 2.491 Å, axial) are longer than the sum of covalent radii (2.36 Å) [15] or the Te–Cl distance in $TeCl_4$, mean 2.311 Å,

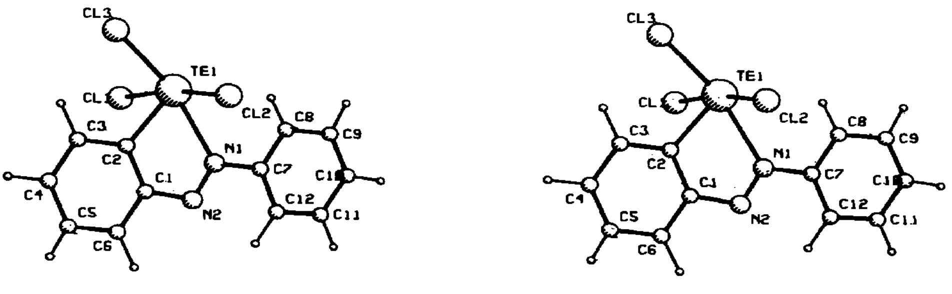


Fig. 1. Stereoscopic view of $C_{12}H_9N_2TeCl_3$ showing the atom numbering.

[19] but agree well with values commonly found for analogous compounds [5,7]. These lengths are, however very much shorter than the sum of the Van der Waals' radii of Te and Cl (4.00 Å), according to Pauling [15], or (3.81 Å) according to Bondi [20], and the Te–Cl bonds can be considered to be essentially covalent in nature. The title compound is monomeric. There are no Te...Cl or Cl...Cl intermolecular contact distances less than the sum of the Van der Waals' radii. In this respect, it is similar to the monomeric 2,6-diacetylpyridine(*C*,*N*,*O*)tellurium(IV) trichloride [7], where, however, the organic ligand is tridentate, unlike the bidentate nature of the ligand in the title compound. In 4-oxo-2-methylpent-2-en-1-yltellurium(IV) trichloride [21] and 8-ethoxy-4-cyclooctenyltellurium(IV) trichloride [5] some association through weak secondary interactions occur, Te...Cl 3.74 and Te...O 3.30 Å in the former and Te...Cl 3.56 Å in the latter. In three other structures $PhTeCl_3$ [8,16] ($4\text{-}EtOPhTeCl_3$) [17] and $ClCH_2CH_2TeCl_3$ [22], association into polymers by relatively strong covalent-type Te–Cl–Te linkages takes place with Te–Cl(bridging) bond lengths in the range 2.72–2.77 Å.

Acknowledgement

One of us (M.A.K.A.) thanks the Iraqi Government for study leave.

References

1 R.E. Cobbledick, F.W.B. Einstein, W.R. McWhinnie and F.H. Musa, J. Chem. Research (S), (1979) 145; J. Chem. Research (M), (1979) 1901.
2 C. Knobler and J.D. McCullough, Inorg. Chem., 16 (1977) 612.
3 J.D. McCullough and C. Knobler, Inorg. Chem., 15 (1976) 2728.
4 J.D. McCullough, Inorg. Chem., 16 (1977) 2318.
5 J. Bergman and L. Engman, J. Organomet. Chem., 181 (1979) 335.
6 T.S. Cameron, R.B. Amero, C. Chan, and R.E. Cordes, Cryst. Struct. Commun., 9 (1980) 543.
7 H.J. Gysling, H.R. Luss, and S.A. Gardner, J. Organomet. Chem., 184 (1980) 417.
8 N.W. Alcock and W.D. Harrison, J. Chem. Soc. Dalton Trans., (1982) 251.
9 R.K. Chadha, J.E. Drake, and M.A. Khan, Can. J. Chem., 62 (1984) 32.
10 P.V. Rolling, J.L. Dill and M.D. Ransch, J. Organomet. Chem., 116 (1976) 46.
11 F.H. Musa, Ph.D. Thesis, University of Aston, 1978.
12 W.H.H. Gunther, personal communication.
13 R.H. Jones and T.A. Hamor, J. Organomet. Chem., 234 (1982) 299.
14 G.M. Sheldrick, SHELX, Program for Crystal Structure Determination, University of Cambridge, 1978.
15 L. Pauling, The Nature of the Chemical Bond, 3rd edit., Cornell University Press, Ithaca, New York, 1960.
16 F.W.B. Einstein and T. Jones, Acta Cryst., B, 38 (1982) 617.
17 P.H. Bird, V. Kumar, and B.C. Pant, Inorg. Chem., 19 (1980) 2487.
18 R.H. Jones and T.A. Hamor, J. Organomet. Chem., 262 (1984) 151.
19 B. Buss and B. Krebs, Angew. Chem. Internat. Edit., 9 (1970) 463.
20 A. Bondi, J. Phys. Chem., 68 (1964) 441.
21 C-K. Huang, D.H. O'Brien, K.J. Irgolic and E.A. Meyers, Cryst. Struct. Commun., 11 (1982) 1593.
22 D. Kobelt and E.F. Paulus, Angew. Chem. Internat. Edit., 10 (1971) 74.