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THE ELECTROCHEMICAL OXIDATION OF 3,4-BENZO-1-TELLURACYCLOPENTANE

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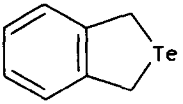
Summary

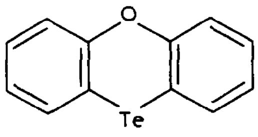
Electrochemical oxidation of 3,4-benzo-1-telluracyclopentane in the presence of tetrabutylammonium salts affords the following deeply coloured salts: $\{C_8H_8Te\}PF_6$, $\{C_8H_8Te\}(I_3)$, $\{C_8H_8Te\}BF_4 \cdot HBF_4$. An unstable perchlorate, assumed to be $\{C_8H_8Te\}ClO_4$, is also described. The IR, ESR and mass spectra of the compounds are discussed. It is concluded that the solids are salt like, but the failure to observe ESR signals may imply a diamagnetic ground state, e.g. involving dimerisation of radical cations. Formally the new compounds are derivatives of tellurium(III).

Introduction

We have recently developed an interest in the role of charge transfer (CT) complexes in organotellurium chemistry [1]. In particular we observed that the 1 : 1 CT complex of 3,4-benzo-1-telluracyclopentane, C_8H_8Te (I) with 7,7,8,8-tetracyanoquindimethane (TCNQ) is probably ionic in the ground state i.e. $\{C_8H_8Te\}^{+}$ $\{TCNQ\}^{-}$.



(I)



(II)

Infra-red spectroscopy and ^{125}Te Mossbauer spectroscopy provided the major support for the formulation [1]. A mass spectroscopic (MS) determination of ionisation potential for I gave the relatively low value of 6.55 eV (1 eV = 96.5 kJ mol^{-1}) [1]. This suggested to us that it might be possible to electrochemically oxidise I to salts of the type $\{C_8H_8Te\}^+ X^-$ were $X^- = PF_6^-$ or BF_4^- for example. It is

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TABLE 1

ANALYTICAL DATA FOR NEW SALTS

Compound	Mp. (°C)	Colour	Analyses (Found (calcd.) (%))	
			C	H
$\{C_8H_8Te\}PF_6$	140	greenish black	25.6 (25.5)	2.18 (2.14)
$\{C_8H_8Te\}BF_4 \cdot HBF_4$	150(d)	black	23.4 (23.7)	2.00 (2.22)
$\{C_8H_8Te\}(I_3)$	–	deep yellow	15.5 (15.7)	1.42 (1.31)
$\{C_8H_8Te\}ClO_4$ [a]	–	black	–	–

[a] Assumed stoichiometry. This compound explodes violently on heating.

known that the radical cation of II, phenoxatellurine may be generated by redox reactions [2]. We found an appearance potential of 8.75 eV for the molecular ion of II although the value of the ionisation potential of II from photo-electron spectroscopy [3] was 7.61 eV, however MS determinations usually give an over estimate.

Experimental and results

3,4-Benzo-1-telluracyclopentane (I) was prepared following the literature [4].

Analytical data are given in Table 1 and some infra-red data are gathered into Table 2.

Electrochemical syntheses

Recrystallised I (10 mmol) in dichloromethane (200 cm^3) was treated with an appropriate supporting electrolyte (20 mmol). In successive experiments the electrolyte was tetra-n-butylammonium hexafluorophosphate, tetrafluoroborate iodide, and perchlorate. The solution was electrolysed between bright platinum electrodes with a spacing of 0.01 m using a constant current of 2 mA. Within a few minutes shiny crystals of the product started to deposit on the anode.

Physical measurements

Infra-red spectra were measured for KBr discs with a Perkin–Elmer 599B instrument over the range 4000–200 cm^{-1}. (N.B. extreme caution was required for

TABLE 2

INFRA-RED DATA (cm^{-1}) FOR NEW SALTS [a]

$\{C_8H_8Te\}PF_6$	$\{C_8H_8Te\}ClO_4$	$\{C_8H_8Te\}BF_4 \cdot HBF_4$	
872v.w	1142s	1110v.br	ν_3, X$^-$
844v.s	1115s	1075v.br	
820sh	1090s	1037v.br	
566s	652s	542br	ν_4, X$^-$
	630s	530br	
2940w	2940w	2940w	$\nu(CH_2)$

[a] Compound I gives $\nu(CH_2)$ at 2920 cm^{-1}.

the perchlorate salt). Mass spectra were determined at 70 eV with an AEI MS9 instrument and ESR measurements were attempted with a JEOL PE-1X spectrometer.

Discussion

Unfortunately, despite numerous attempts no crystals suitable for crystallographic study could be isolated from any of the preparations. We were, however, able to examine the materials by a range of standard spectroscopic measurements.

Infra-red spectroscopy shows the hexafluorophosphate material to contain anionic PF_6^-, the positions of ν_3 and ν_4 being consistent with this interpretation [5], since the single sharp ν_4 makes it unlikely that the splitting of ν_3 reflects cation–anion interaction. By contrast, both ν_3 and ν_4 for the perchlorate are cleanly split and this could indeed imply a weak cation–anion interaction. However, due to the temperamental nature of this material, our other data are necessarily limited. The tetrafluoroborate salt is remarkable for the breadth of the regions of absorption associated with ν_3 and ν_4. Given that the stoichiometry is also different, we feel that interpretation in terms of two types of BF_4 group is justified. Skeletal modes of the telluride (I) are altered by electrochemical oxidation. Generally the bands are sharper and are shifted to higher frequency. We particularly note a shift of +20 cm^{-1} for $\nu(CH_2)$ which seems reasonable if an element of positive change is localised on tellurium.

None of the compounds gave ESR spectra. This may be a consequence of a large spin orbit coupling constant (λ_{Te} 0.49 eV) leading to increased line width, or it could imply a diamagnetic ground state achieved by dimerisation of the radical cations.

The mass spectra of the salts show $\{C_8H_8Te\}^+$ as the ion of greatest m/e. The tetrafluoroborate gives a major peak at $m/e = 68$, 67 the isotropic ratio of which is correct for BF_3. In addition a line at $m/e = 20$ is attributed to HF, thus providing support for the proposal that HBF_4 may crystallise with the tetrafluoroborate salt and also helping to explain the broad IR spectra.

We believe that the evidence as it stands provides support for the view that a range of new salts $\{C_8H_8Te\}^+ X^-$ have been prepared. The molecular complexity remains a matter for speculation, but it is of interest to note that the new compounds are formally examples of tellurium showing the rare oxidation state of tellurium(III).

Acknowledgment

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